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In the wet-limestone process for the removal of sulfur dioxide from power-plant stack gases, the gases are scrubbed with an aqueous suspension of finely ground limestone and the dissolution of the limestone is the rate-limiting step. An organic acid could be added to the system to accelerate the dissolution of the limestone and thereby increase the scrubber efficiency. The rate of dissolution can be increased by adding an acid that is stronger than carbonic acid and weaker than sulfurous acid. In a search for a suitable additive, measurements were made of the solubility of calcium and magnesium carbonates in solutions of 27 weak organic acids that were selected on the basis of their low cost and availability from a large number of acids that meet the primary requirements. From these results, four acids--benzoic, phthalic, adipic, and glycolic--were chosen for further study of their physicochemical properties that would affect their potential usefulness in a scrubber system.

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1137

SULFUR OXIDE REMOVAL FROM POWER PLANT STACK GAS

study of the effect of organic acids on the wet – limestone scrubbing process

Tennessee Valley Authority
Division of Chemical Development
Fundamental Research Branch

Sulfur Dioxide Removal From Power Plant Stack Gas

STUDY OF THE EFFECT OF ORGANIC ACIDS ON THE WET-LIMESTONE SCRUBBING PROCESS

By

J. D. Hatfield, Y. K. Kim, and R. C. Mullins

Prepared for

Office of Air Programs
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Muscle Shoals, Alabama 35660
February 24, 1972

STUDY OF THE EFFECT OF ORGANIC ACIDS ON THE WET-LIMESTONE SCRUBBING PROCESS

SUMMARY

The dissolution of limestone is one of the rate-limiting steps in the process for removal of sulfur dioxide from stack gases by scrubbing with limestone slurry. The rate of dissolution can be increased by adding an acid that is stronger than carbonic acid ($K_1 = 4.4 \times 10^{-7}$) and weaker than sulfurous acid ($K_1 = 1.3 \times 10^{-2}$). In a search for a suitable additive, measurements were made of the solubility of calcium and magnesium carbonates in solutions of 27 weak organic acids that were selected on the basis of their low cost and availability from a large number of acids that meet the primary requirements. From these results, four acids--benzoic, phthalic, adipic, and glycolic--were chosen for further study of their physicochemical properties that would affect their potential usefulness in a scrubber system. The acids suggested in the literature (U. S. Patent 3,632,306, January 4, 1972) for this purpose--formic, acetic, and propionic--were considered unsuitable.

A high degree of acid stability was demonstrated by tests under conditions much more drastic than those likely to be encountered in scrubbing operations. Gas mixtures containing as much as 67% SO_2 and 33% O_2 were passed through aqueous solutions of the acids at 75°C for as long as 59 hours without producing any change in the ultraviolet absorption patterns of the solutions. Molten acids exposed to similar gas mixtures rich in SO_2 and O_2 showed the same ultraviolet peaks as solutions of the untreated melts.

The solubilities of calcium and magnesium carbonates in 0.05, 0.1, and 0.2% solutions of each of the four acids were measured at 25°C and in 0.1% solutions at 50°C. Within experimental error the solubilities at the two temperatures were the same. The concentration of the acid is the limiting factor up to 50°C. Saturation solubilities at 25° and 50°C of the calcium and magnesium salts of the four acids were obtained also. The solubilities of the salts of the monobasic acids increased with rising temperature and those of the dibasic acids decreased. Arranged in the order of the calcium concentration in the saturated solutions at 50°C they are glycolic > benzoic > adipic > phthalic. Phthalic acid gives only about one tenth the concentration of calcium as the other acids.

Measurements were made of the pH of both the solutions formed by dissolution of the carbonates and the saturated solutions of the calcium salts. The solubility and pH data were analyzed by a computer program to evaluate the concentration of the species in the solutions and to determine the stability constants of the complexes. No consistent values of dissociation constants for complexes of calcium or magnesium with phthalic, adipic, or glycolic acid were obtained. The value for the equilibrium constant of the weak complex $CaBz^+$ was calculated to be

$$\log K^* = -2.13 \pm 0.15 \text{ at } 25°C$$

$$\log K^* = -1.0 \pm 0.5 \text{ at } 50°C$$

Measurements were made of the ultraviolet absorptions of calcium benzoate solutions, and the activities of the calcium ion were measured with the calcium ion specific electrode. The results were treated by Job's method of continuous variation in an attempt to determine whether there is an aqueous complex of calcium benzoate. If such a complex exists it is too weak to be detected by the methods of measurement used.

The vapor pressure of a benzoic acid solution (1.6 grams/liter) was measured at three temperatures by a dynamic method after difficulties with vapor absorption on the equipment were overcome. The data can be expressed by the relation

$$\log P = 9.20 - 4781/T$$

where P is pressure, atmosphere, and T is temperature, °K. The relation is consistent with the accepted value for the heat of vaporization. Calculations were made, from the data and published values for ionization constants and activity coefficients, of the vapor pressure over this concentration of solution for a range of temperature and pH The results indicate that the loss of acid as vapor under scrubbing conditions would be relatively low.

The effect of the acids on the oxidation of sulfite to sulfate was studied also. Exploratory tests in the sodium system showed that the acids promote oxidation. In the calcium system at 50°C and pH 4, 0.1 M solutions of the acids inhibited the oxidation of sulfite by pure oxygen in the order benzoic > glycolic > phthalic > adipic. From plots of the rates of oxidation for the 0.1 M solutions the first-order rate constants were determined. Measurements were made of the effect of pH on the oxidation of calcium sulfite without an organic acid and the relationship between oxidation rate and pH under the test conditions was shown to be linear between pH 3 and 4.5. The data from the oxidation tests were processed by a computer program to calculate the species concentration and activities from the constants and activity coefficients suggested by the Radian Corporation.

The temperature dependence of benzoate equilibrium constants in the form used by Radian Corporation (PB 193 029)

$$\log K = -AT^{-1} - B \log T - CT + D$$

are shown in the tabulation

	A	B	C	D
$HBz \rightleftarrows H^+ + Bz^-$	804.7	0	0.0090476	1.192
$CaBz^+ \rightleftarrows Ca^{++} + Bz^-$	4354.5	0	0	12.475
$HBz(g) \rightleftarrows HBz(aq)$ (Henry's law)	-4500.	0	0	-10.27

These constants, when incorporated into the Radian equilibrium program, will describe the properties of slurries containing benzoic acid when used in the wet limestone scrubbing process.

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STUDY OF THE EFFECT OF ORGANIC ACIDS ON THE WET-LIMESTONE SCRUBBING PROCESS

INTRODUCTION

In the wet-limestone process for the removal of sulfur dioxide from power-plant stack gases, the gases are scrubbed with an aqueous suspension of finely ground limestone and the dissolution of the limestone is the rate-limiting step. It was proposed that an organic acid be added to the system to accelerate the dissolution of the limestone and thereby increase the scrubber efficiency, and this report covers an investigation of the use of organic acids for this purpose.

The work covered by this report was intended to extend over 2 years, beginning July 1, 1970. Shortly after the end of the first year, however, financial support for the work was withdrawn and, except for completing work in progress, the research was terminated. This report covers work done in the period July 1, 1970, to September 30, 1971.

In the work covered by this report, several phases of the investigation were carried out simultaneously, and each portion of the research was reported as it was completed, so that in chronological order the reports would be difficult to follow. The monthly reports have been rearranged to combine all the work on each phase in a single section, and the dates on which the results were reported are retained.

In lieu of a completion report, this report is a compilation of the monthly progress reports on the work. Since each progress report was essentially a complete unit, the tables and figures were numbered separately for each report. These numbers are retained here, and, since the tables and figures are inserted in the text in the order in which they are referred to, the lack of unified series of numbers for the tables and for the figures should not be confusing.

SURVEY OF WEAK ORGANIC ACIDS

The rate-determining step in the wet limestone scrubbing process for the removal of SO_2 from stack gases is the dissolution of the limestone in the scrubbing slurry. The dissolution rate is affected by the particle size and surface area of the limestone, the source and mineralogical properties of the limestone, the temperature, and the acidity of the slurry. The most important factor that affects the dissolution rate of a limestone is its solubility in the liquid phase of the slurry which gives the driving force for dissolution. The calcium and magnesium salts of many organic acids are soluble and the addition of organic acids to the scrubbing slurry should improve the wet limestone scrubbing process. The Applied Research Branch has demonstrated improvement by the use of benzoic acid, and some of the lower aliphatic acids have likewise shown promise in improving the process.

Measurements were made of the solubilities of calcium and magnesium carbonates in solutions of selected organic acids and the absorbances of the solutions in the ultraviolet region were determined.

Several of the organic acids from the list prepared by the Applied Research Branch were chosen to test their solubilization of $CaCO_3$ and $MgCO_3$. The acids were selected to give a wide variation in formula and structure and include aliphatic and aromatic acids, acids with different chain lengths, with different substitutions of other groups for hydrogen, with different degrees of saturation, and with different numbers of carboxy groups in the molecule.

One gram of the organic acid (or 1 ml. if the acid is liquid) was added to 100 ml. of water, the pH was measured, and 5 grams of reagent grade $CaCO_3$ or $MgCO_3$ was added to the solution or mixture. The mixtures were allowed to stand at room temperature with shaking at irregular intervals. The pH was measured and 10-ml. aliquots of the clear solution were taken after 3 days and after one week. The results are shown in the table.

For a given weight of acid, the aliphatic acids were most effective in solubilizing calcium or magnesium carbonate and the lower molecular weight acids were superior to the acids of higher molecular weight. The substitution of chlorine, hydroxy, or phenyl groups for hydrogen decreased the solubility, but apparently unsaturated acids were slightly more effective than their saturated analogues. The polycarboxylic acids were effective solubilizers with the exceptions of oxalic, tartaric, and citric acids for calcium. The aromatic acids were less effective than the lower aliphatic acids, and any substitution on the benzene ring decreased the solubility of the cation.

Use of Organic Acids in the Dissolution of Calcium and Magnesium Carbonates

Acid	Formula	pH of acid solution	Sol., Ca, wt. %, after 3 days	after 7 days	After 7 days mole ratio acid:Ca[b]	pH	Sol., Mg, wt. %, after 3 days	after 7 days	After 7 days mole ratio acid:Mg[b]	pH	Price dollars/lb.
Aliphatic monocarboxylic acids											
Formic	HCOOH	2.30	0.48	0.54	1.7	7.00	0.40	0.41	1.4	7.60	0.147
Acetic	CH_3COOH	2.30	0.32	0.37	1.9	7.20	0.31	0.31	1.4	7.65	0.09
Chloroacetic	$ClCH_2COOH$	2.15	0.21	0.21	2.0	7.15	0.20	0.20	1.5	7.85	0.21
Glycolic	$HOCH_2COOH$	2.40	0.22	0.25	2.1	7.40	0.24	0.27	1.2	7.50	0.10
Phenylacetic	$C_6H_5CH_2COOH$	2.70	0.13	0.15	2.0	7.40	0.14	0.13	1.4	8.15	0.68
Propionic	C_2H_5COOH	2.90	0.28	0.28	1.9	7.20	0.27	0.21	1.6	7.75	0.147
Lactic	$CH_3CHOHCOOH$	2.50	0.21	0.23	1.9	6.90	0.21	0.21	1.3	7.70	0.275
Butyric	C_3H_7COOH	2.90	0.22	0.21	2.2	6.65	0.23	0.21	1.3	7.50	0.33
Caproic	$C_5H_{11}COOH$	3.00	0.17	0.17	2.0	6.15	0.13	0.12	1.7	7.90	
Gluconic	$CH_2OH(CHOH)_4COOH$	2.80[a]	0.06	0.06	3.4	7.00	0.06	0.08	1.6	8.00	0.145
Acrylic	$CH_2=CHCOOH$	2.60	0.31	0.31	1.8	6.60	0.23	0.21	1.6	7.70	0.31
Oleic	$CH_3(CH_2)_7C=C(CH_2)_7COOH$	3.80[a]	0.01	0.01	16.7	6.60	0.03	0.03	3.4	8.45	0.23
Aliphatic polycarboxylic acids											
Oxalic	$COOHCOOH$	1.75	0.01	0.01	44.4	7.70	0.13	0.08	3.4	8.35	0.22
Succinic	$COOHCH_2CH_2COOH$	2.30	0.27	0.32	1.1	7.35	0.29	0.30	0.69	7.80	0.62
Tartaric	$COOHCHOHCHOHCOOH$	2.25	0.01	0.01	26.7	7.70	0.24	0.26	0.62	7.85	0.415
Malic	$COOHCHOHCH_2COOH$	2.40[a]	0.09	0.09	3.3	7.60	0.22	0.24	0.76	8.40	0.315
Fumaric	$COOHCH=CHCOOH$	2.35[a]	0.25	0.28	1.2	7.30	0.28	0.27	0.78	8.00	0.225
Maleic	$HO_2CCH=CHCO_2H$	1.95	0.23	0.31	1.1	7.25	0.31	0.30	0.70	7.70	0.48
Adipic	$COOH(CH_2)_4COOH$	2.80	0.28	0.28	1.0	7.20	0.26	0.21	0.79	7.80	0.18
Citric	$(COOHCH_2)_2COOHCOOH$	2.25	0.02	0.02	10.	7.80	0.24	0.24	0.53	8.50	0.33
Aromatic acids											
Benzoic	C_6H_5COOH	2.75[a]	0.14	0.17	1.9	7.35	0.04	0.13	1.5	8.20	0.215
Salicylic	HOC_6H_4COOH	2.60[a]	0.11	0.14	2.1	7.35	0.21	0.13	1.4	8.15	0.425
P-Amino benzoic	$NH_2C_6H_5COOH$	3.50[a]	0.15	0.15	1.9	7.40	0.14	0.14	1.5	8.00	1.72
Dinitro benzoic	$(NO_2)_2C_6H_3COOH$	2.80[a]	0.09	0.10	1.9	7.45	0.09	0.09	1.3	8.10	
Gallic	$(HO)_3C_6H_7COOH$	2.85	0.11	0.11	2.1	6.20	0.12	0.11	1.3	8.15	2.65
Phthalic	$C_6H_4(COOH)_2$	2.45[a]	0.12	0.06	4.0	7.60	0.22	0.21	0.70	8.05	0.12
α-Naphthoic	$C_{10}H_7COOH$	3.75[a]	0.02	0.01	23	6.70	0.08	0.06	2.3	8.30	

[a] 1 gram of acid did not completely dissolve in 100 ml. H_2O.

[b] Based on solubilities after 1 week, assuming all acid dissolved.

The columns in the table that show the mole ratio of acid used to metal solubilized indicate that one calcium atom reacts with two carboxy groups for those acids having appreciable solubilizing power; for magnesium the number of carboxy groups required is somewhat less--approximately 1.5. On the basis of solubility alone, it is concluded that the best additives are those of low molecular weight, since a given weight of the additive would contain more acidic groups to react with the calcium or magnesium. Other factors such as cost and losses due to volatility and decomposition under scrubbing condition need to be considered, however.

Of the aliphatic monobasic acids, acrylic, glycolic, and chloroacetic acids appear promising, provided they are stable and have sufficiently low vapor pressures under scrubbing conditions. It is probable that chloroacetic acid may hydrolyze to glycolic acid under scrubbing conditions; this type of reaction may occur with any halogen substituted acid. The dicarboxylic acids that appear promising are adipic, succinic, maleic, and fumaric, provided they are stable and nonvolatile. Benzoic appears to be the most promising aromatic acid, although phthalic acid is very effective for magnesium. Since phthalic acid is inexpensive it should be tested for calcium at the scrubbing temperature of 55° C.

Ultraviolet Absorbance of Benzoic Acid: Since the Applied Research Branch has shown the effectiveness of benzoic acid in improving the wet scrubbing process, the stability of the additive with continued use is important to the economics of the process. A method for rapid analysis of the additive in the solution phase of the slurry is being tested with the Cary 17 UV spectrometer.

The absorbance spectra of benzoic acid at room temperature showed two distinct peaks at 193 mμ and 230 mμ and a broad shoulder at about 270 mμ. The molar absorptivity of benzoic acid was found to be 4.015×10^4 and 9.964×10^3 at 193 mμ and 230 mμ, respectively. Plots of the absorbances at the two peaks against the concentration in solution, Figure 1, show that Beer's law is valid for the system from 0 to 5 ppm benzoic acid. The absorbances were only slightly affected by the pH of the solution when it was varied by the addition of calcium or sodium hydroxide. Thus by diluting the solution to this concentration range we can measure the benzoate concentration very accurately, and can detect any loss of the acid by decomposition or vaporization.

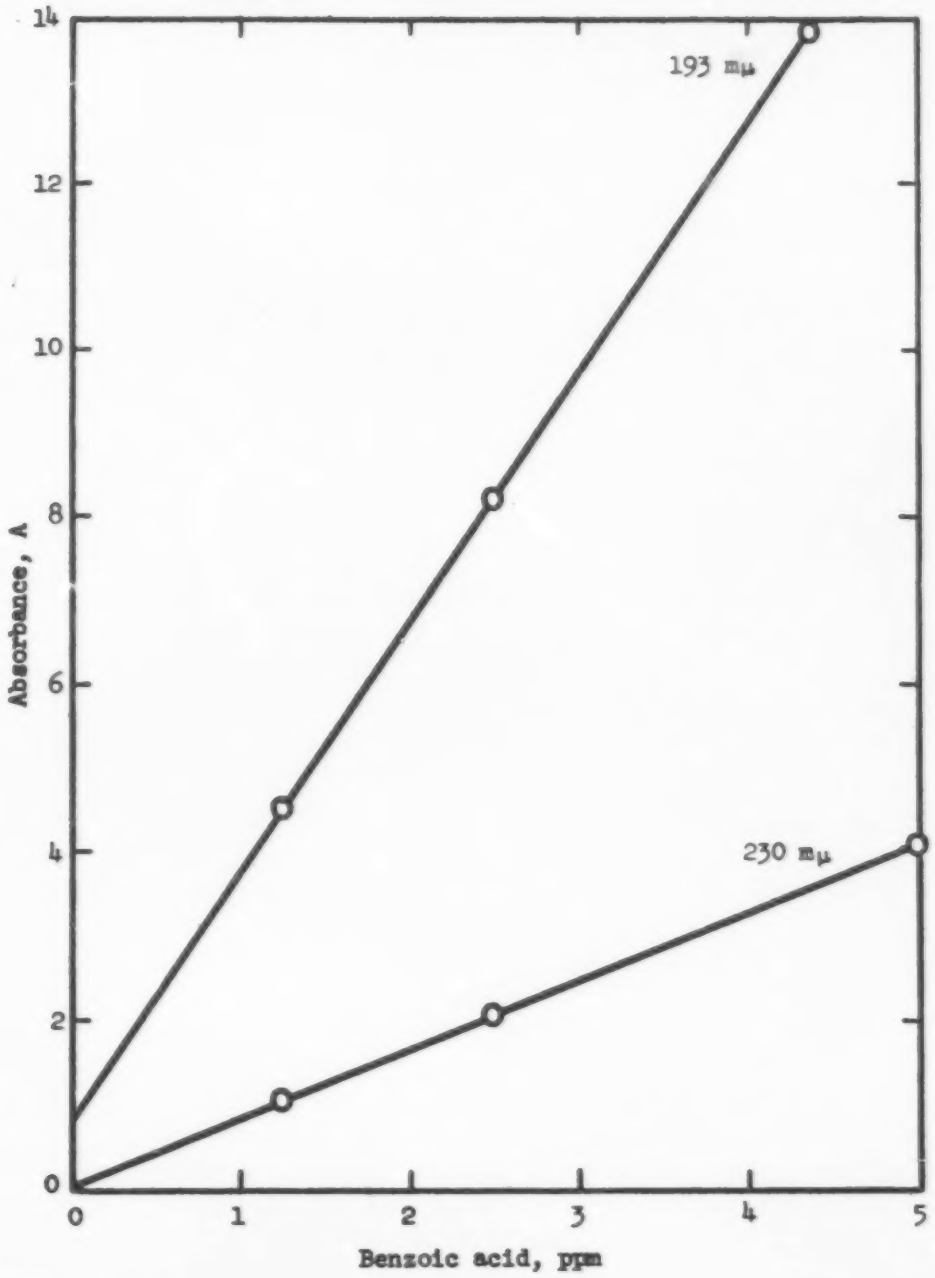


Figure 1

Calibration Curves for Analysis for

Benzoic Acid With Cary 17 UV Spectrometer

(J. D. Hatfield, Y. K. Kim, V. L. Bulger)

July 1970 - FR

Other Absorption Studies: The two absorption peaks of benzoic acid are probably due to the species Bz^- and HBz^0 that exist in solution. The ratio of these species is related to the pH of the solution through the ionization constant, K,

$$K = [Bz^-][H^+]/[HBz] \qquad (3)$$

This implies that careful control of pH is needed to measure the concentration of benzoic acid in scrubber solutions as well as the effects of cations.

A series of solutions containing a constant amount of benzoic acid, 4×10^{-4}M, and increasing amounts of base--NaOH or $Ca(OH)_2$--were prepared; the ionic strength of each solution was maintained at about 0.1M with sodium perchlorate. These simulated titration curves are shown in Figure 4, and the absorbances at 193 and 227 μm are shown in Figure 5. There was very little difference between the "titration" curves with NaOH and those with $Ca(OH)_2$. The absorbance at 193 μm increased steadily as base was added until the equivalent point was reached, after which the increase was slower and more erratic. There was a slight but distinct difference between the absorbance of solutions containing sodium and of those containing calcium. The absorbance at 227 μm decreased as base was added and then became approximately constant beyond the equivalence point.

These results will be evaluated further to assess the effect of cation constituent on the absorbances, and the effect of solution composition in the analysis of benzoate by ultraviolet absorption. The data also will be analyzed to determine the ionization constant of benzoic acid at 25°C and at an ionic strength of 0.1, and attempts will be made to evaluate hypotheses concerning complexes of calcium and benzoate ions and to obtain the magnitude of the strength of such complexes to explain the experimental data.

Similar studies will be made with magnesium benzoate and with calcium and magnesium salts of adipic, glycolic, and phthalic acids.

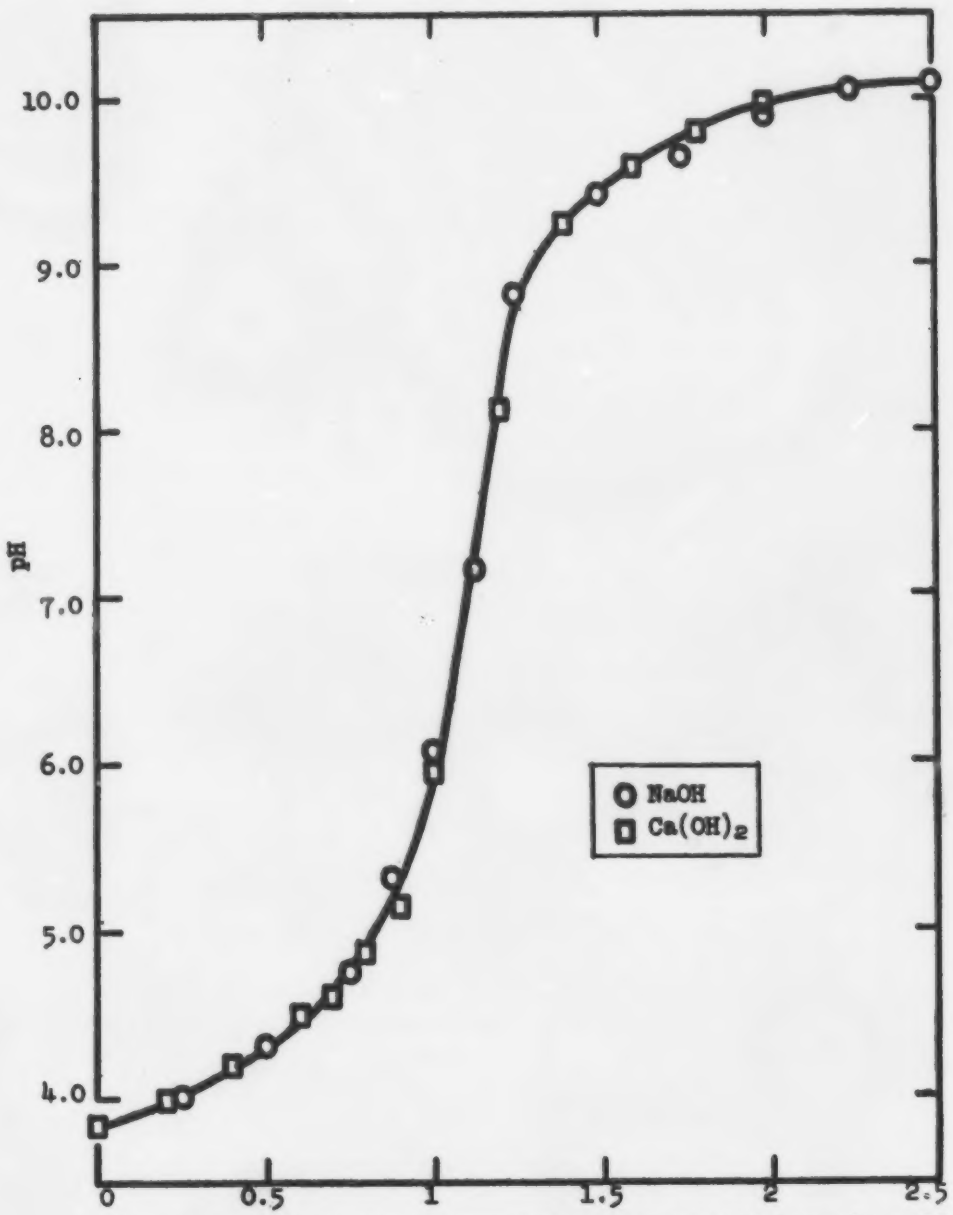


Figure 4

Titration Curve of Benzoic Acid

With Sodium and Calcium Hydroxide

December 1970 - FR

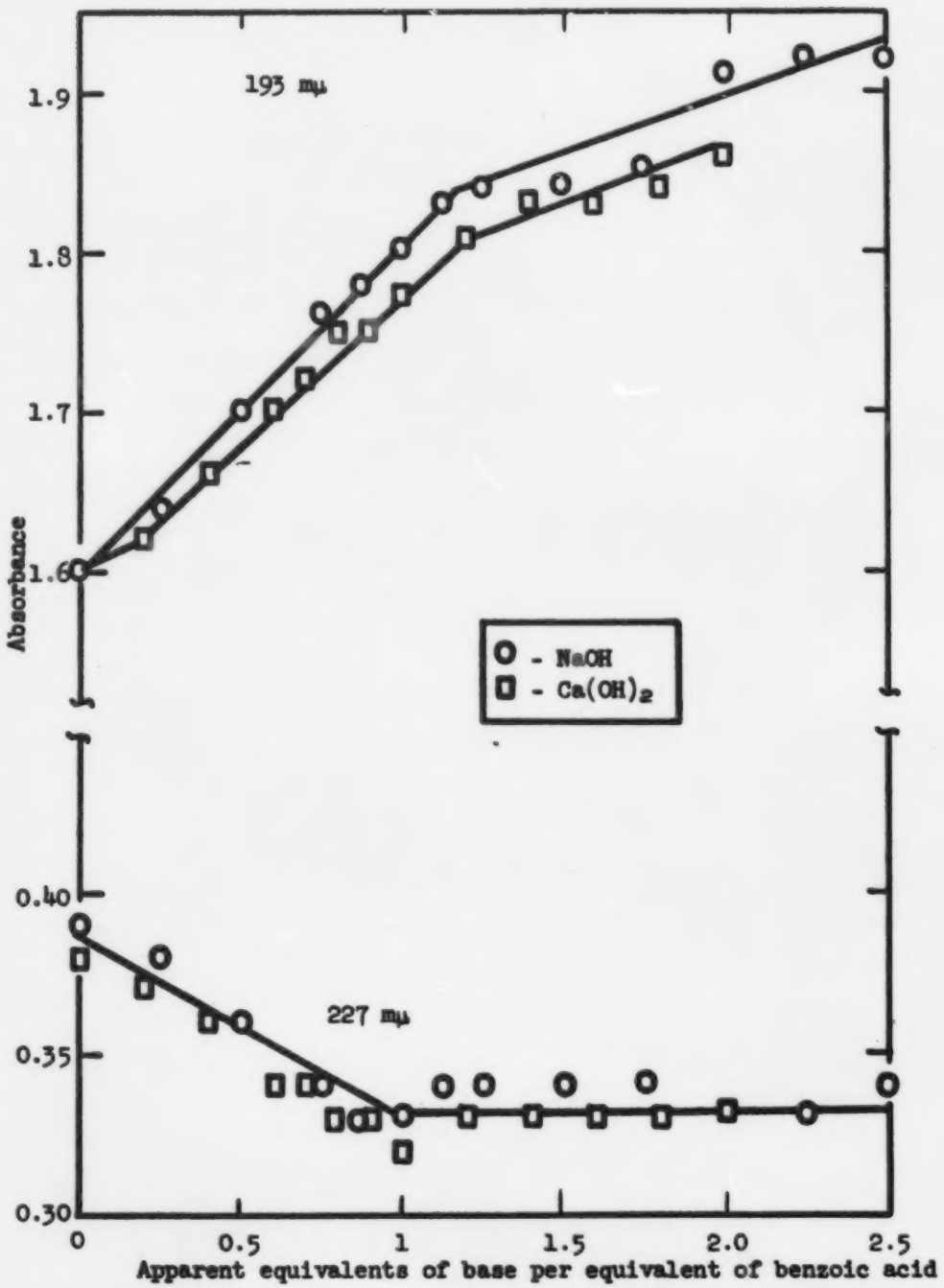


Figure 5

Ultraviolet Absorbance of Calcium and

Sodium Benzoate Solutions

(J. D. Hatfield, Y. K. Kim,
R. C. Mullins)

December 1970 - FR

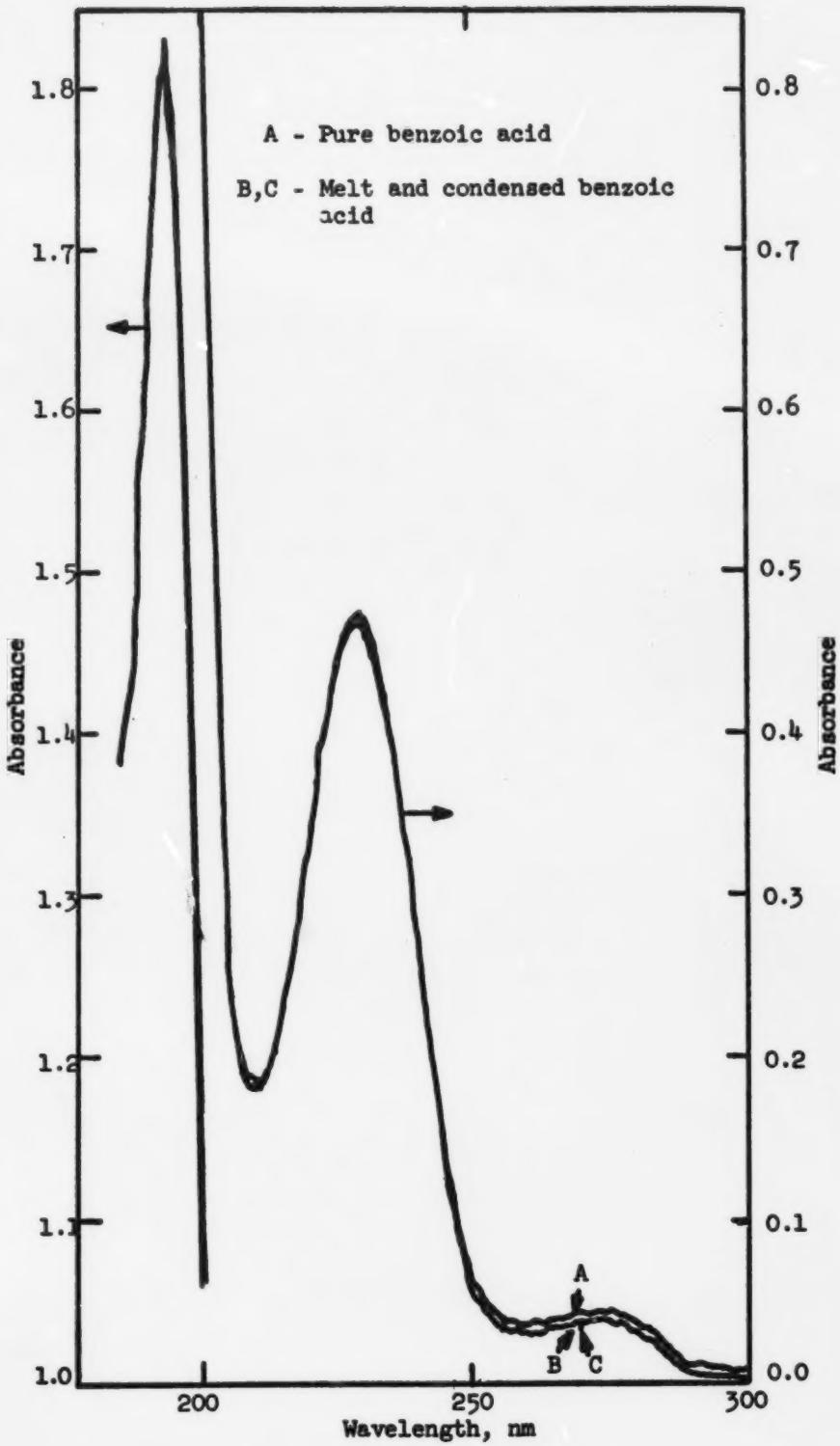
STABILITY OF ORGANIC ACIDS UNDER SCRUBBING CONDITIONS

Stability of Benzoic Acid: The stability of benzoic acid was studied under conditions more drastic than those expected to be encountered under scrubbing conditions to accelerate its decomposition or oxidation and to identify any products of decomposition that may be formed.

In one test, about 700 ml of a 0.3% benzoic acid solution was placed in a 1-liter flask maintained at 75°C in a water bath. A gas mixture (50% SO_2, 25% O_2, and 25% N_2) was passed through a coarse fritted glass into the liquid at a rate of 200 ml/min. Samples of the solution were withdrawn at regular intervals for determination of the ultraviolet absorption pattern. After 51 hours of aeration with the gas mixture at 75°C, the ultraviolet absorption of the solution was compared with that of pure benzoic acid. The absorption peaks at 193 and 227 nm were unchanged from the treatment, and there were no new absorption peaks. (The wave lengths were erroneously listed in the December report as μm; these should be nm or mμ).

In another test, about 20 grams of pure benzoic acid was placed in a scrubbing tube, and the assembly was placed in a furnace at 136° ± 2°C to give a molten product (benzoic acid melts at 122°C). A gas mixture (67% SO_2, 33% O_2) was passed through a fritted glass into the melt at the rate of 45 cc/minute. Some benzoic acid crystals condensed in the cool portion of the apparatus during the run. After bubbling the gas through the molten benzoic acid for 18 hours, the assembly was removed from the furnace and the melt was allowed to solidify at room temperature. Samples of the same weights of the melt, the condensed acid on the wall of the scrubbing tube, and pure benzoic acid were dissolved in the same amounts of water, and the ultraviolet absorption patterns and peak heights of the three solutions were determined as shown in the figure. No new absorption peaks were found in the melt or in the condensate, and these two materials were identical in purity with the benzoic acid.

These tests, made under more severe conditions than would be encountered in pilot-plant operation, indicate that benzoic acid is quite stable and is not decomposed by SO_2 and oxygen.



Ultraviolet Absorption of Benzoic Acid

January 1971 - FR

Stability of Organic Acids: Accelerated measurements were made of the stability of the 4 organic acids--benzoic, phthalic, adipic, and glycolic--being studied as additives to the wet-limestone scrubbing process. The results for benzoic acid were reported in January; this report describes tests of the other three acids and summarizes all the results. All tests were made under conditions more drastic than those expected to be encountered under scrubbing conditions in order to reduce the time required for the tests and to identify any products of decomposition.

In one series of tests, the organic acids were dissolved in water, and the SO_2 gas mixture was bubbled through a coarse fritted glass into the solution which was maintained at constant temperature in a water-bath. Conditions of the tests for each organic acid are summarized in Table I. In another series of tests, the pure acid (solid) was placed in the bottom of a scrubbing tube, the assembly was heated in a furnace at a fixed temperature above the melting point, and the gas mixture was passed through a fritted glass into the melt. The conditions of these tests also are summarized in Table I. Glycolic acid was not treated in this manner because it was available only as a 70% aqueous solution.

In the first series of tests, the solutions after scrubbing had a strong odor of SO_2 and exhibited strong peaks of ultraviolet light absorption at 188 and 207 nm which interfered with the organic acid absorbance measurements. The odors and the absorbance peaks due to SO_2 were completely eliminated by boiling for about 10 minutes on a hot plate. The ultraviolet light absorbances of the acid solutions were measured after this treatment and after appropriate dilution.

Phthalic, adipic, and glycolic acids, after treatment to expel the SO_2, showed essentially the same spectrum as the pure acids at the same concentration (Figures 1, 2, 3). The slight differences between the absorption curves for the treated solutions of phthalic and glycolic acid and the reference curves probably are due to the loss by evaporation of the acid during heating to expel the SO_2 from the solutions; there appeared to be little or no loss of adipic acid in the treatment. No new absorbance peaks were observed in any of the acids.

TABLE I

Reaction Conditions for the Organic Acid Stability Measurement

Acid	Time, hours	Temp., °C	Sample	Gas compn., parts by volume SO_2	O_2	N_2	Flow rate, cc/min
			Tests with solutions				
Benzoic	51	75	700 ml, 0.3% soln.	2	1	1	200
Phthalic	53	75	400 ml, 0.1% soln.	2	1	0	120
Adipic	59	75	500 ml, 2% soln.	1	1	0	40
Glycolic	28	55	200 ml, 70% soln.	2	1	0	45
			Tests with melts				
Benzoic	18	136	20 grams	2	1	0	45
Phthalic	0.5	212	60 grams	2	1	0	45
Adipic	10	162	30 grams	2	1	0	45

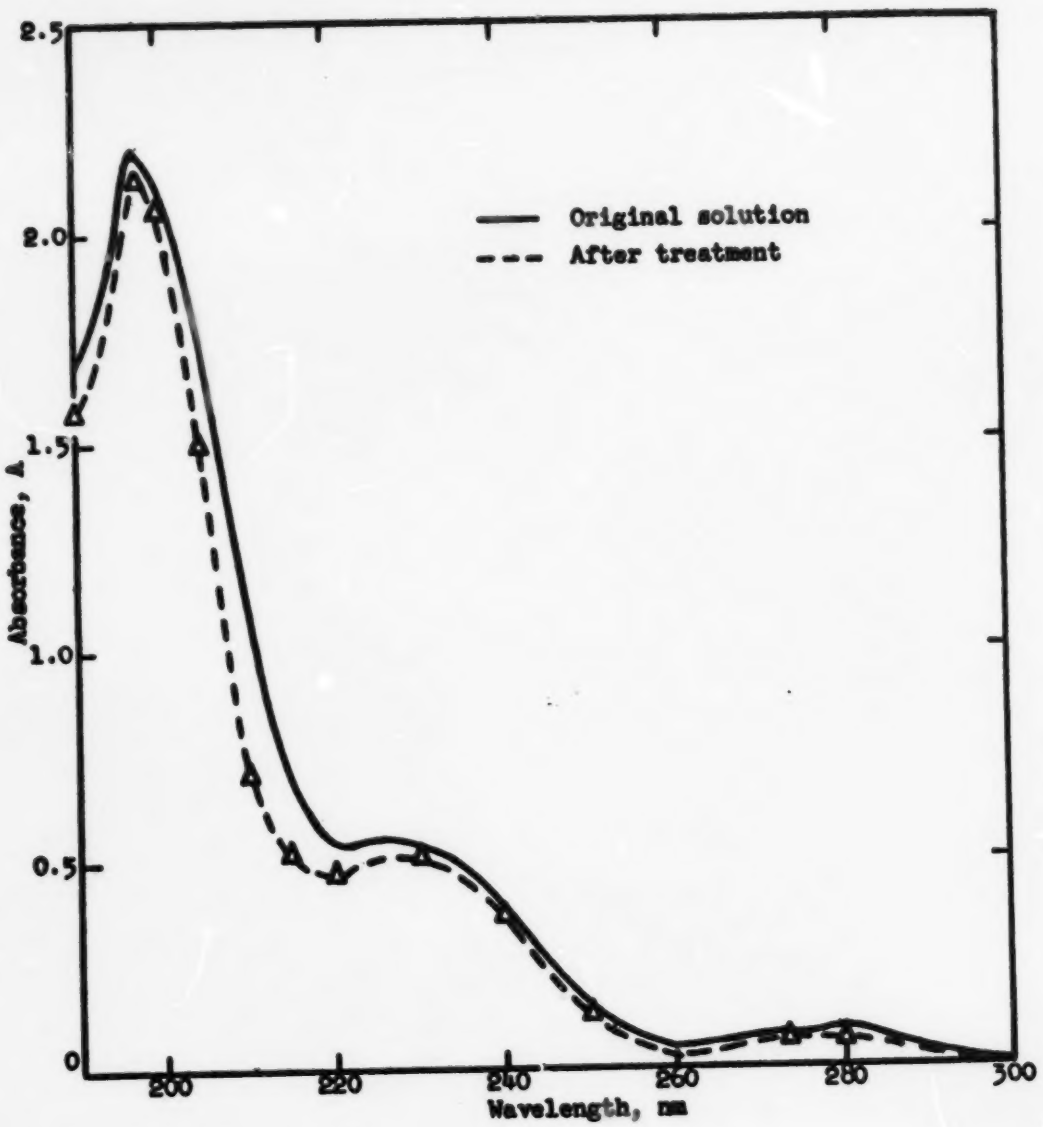


Figure 1

Ultraviolet Absorbance of Phthalic Acid

(0.1% solution in a 1-mm cell)

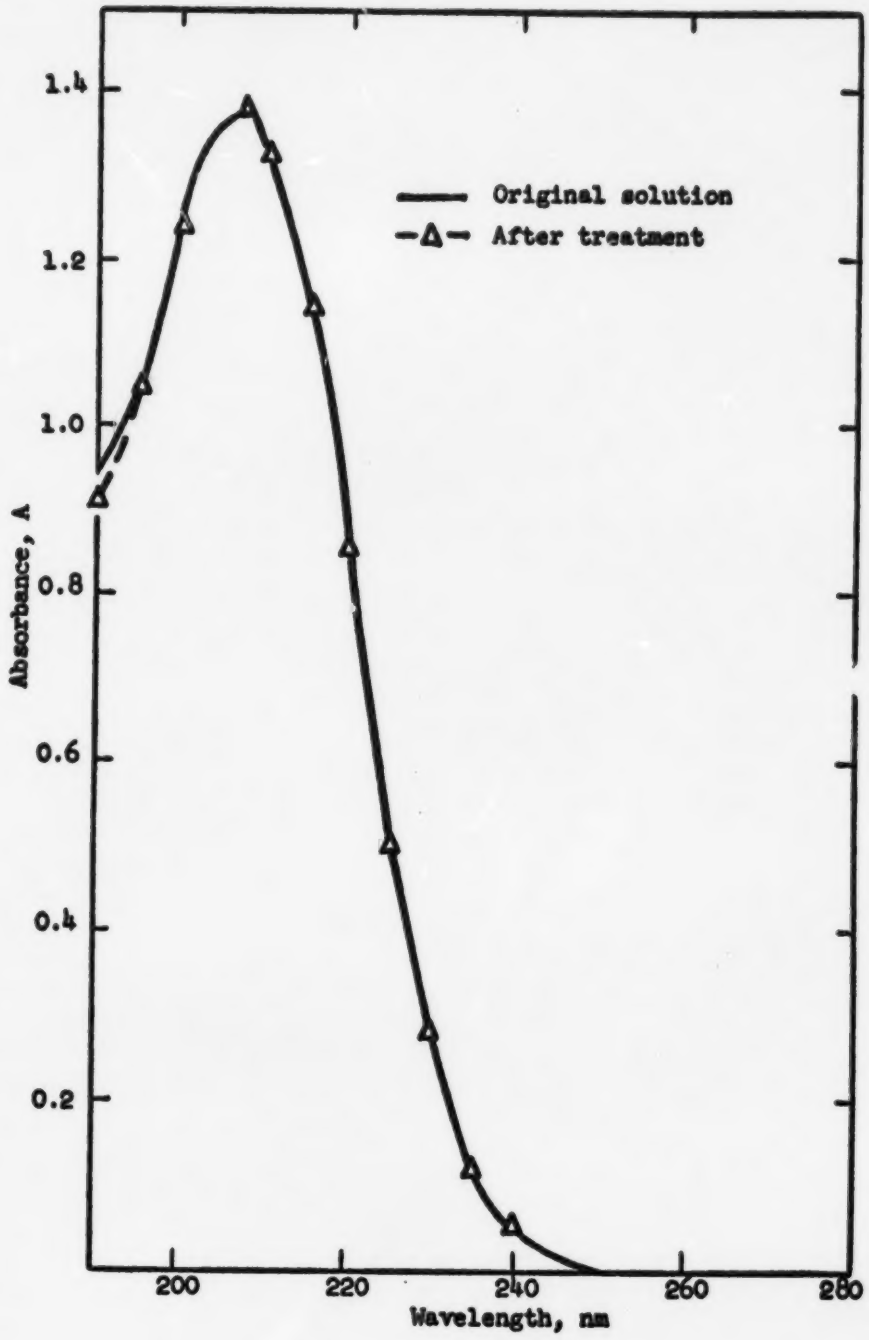


Figure 2

Ultraviolet Absorbance of Adipic Acid

(2% solution in a 1-mm cell)

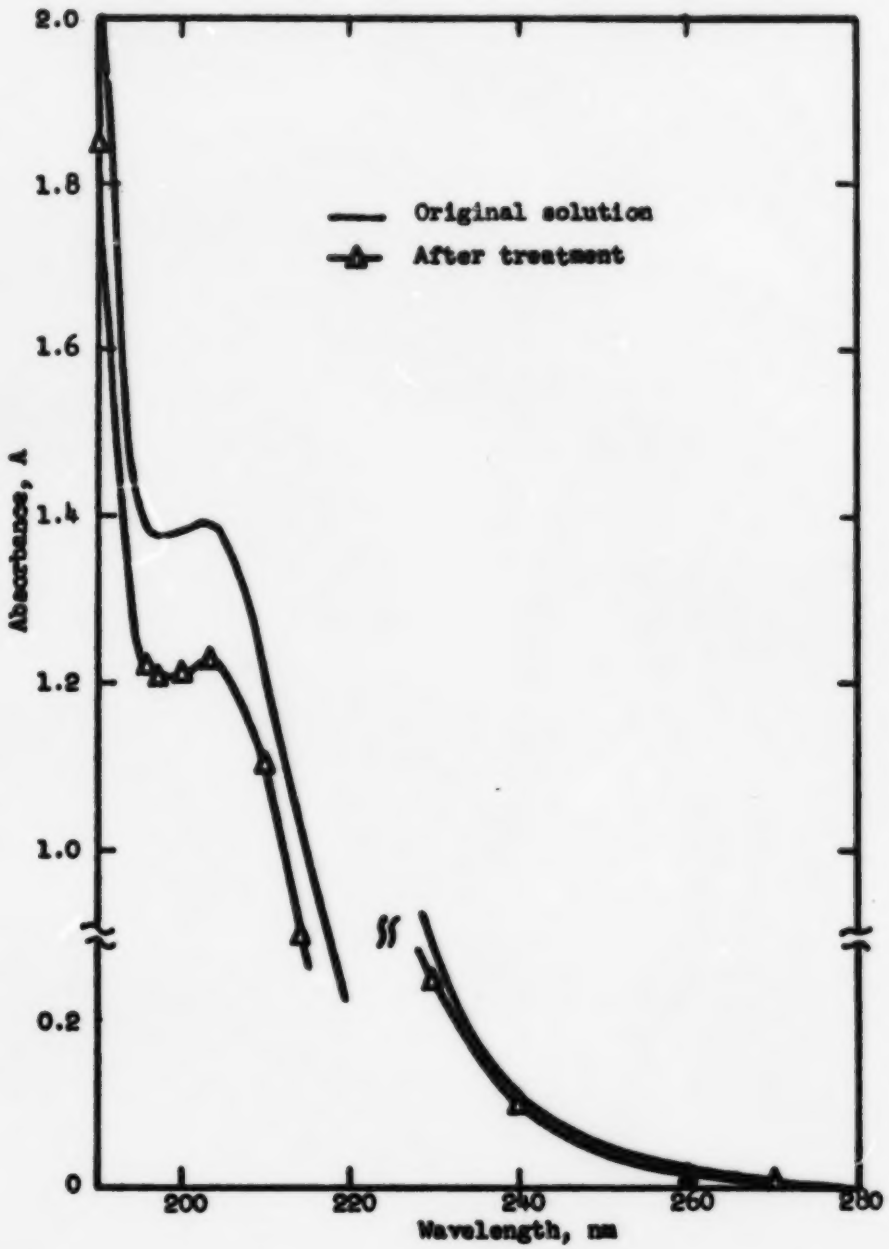


Figure 5

Ultraviolet Absorbance of Glycolic Acid

(1.4% solution in a 1-mm cell)

In the second series of tests, phthalic acid did not melt until the temperature reached 212°C, and the vapor pressure of the phthalic acid was so high that the condensing vapor completely blocked the exit tube and the test was terminated after 30 minutes. Adipic acid became grayish in color after 10 hours at 162°C but its ultraviolet absorption pattern was identical with that of pure adipic acid. No weight change was observed during the tests and no organic compound that absorbed ultraviolet light was detected in the exit-gas scrubbing tube.

The results of this study indicate that benzoic, phthalic, adipic, and glycolic acid are stable compounds in the presence of SO_2 and O_2 under conditions more severe in temperature and concentration than would be encountered in the wet-limestone scrubbing process. The principal losses of the organic acids would be from vaporization and these will be calculated from vapor pressure measurements in progress. However, there is a possibility of organic acid degeneration by the accumulation of highly oxidizing ions and radicals in a closed-loop system; no plans are made to study this possibility at the present time. (J. D. Hatfield, Y. K. Kim)

SOLUBILITY STUDIES WITH SELECTED ORGANIC ACIDS

Measurements at 25°C

The solubility at 25°C of calcium and magnesium carbonates in solutions of the four organic acids being considered as additives for the wet limestone scrubbing of SO_2 are shown in Table I. Available acids used for the tests were B & A reagent-grade benzoic, Fisher pure flake phthalic anhydride, Fisher certified adipic, and Eastman technical-grade glycolic (70% aqueous solution). The benzoic acid and phthalic anhydride were assayed by comparing the ultraviolet absorption of their solutions with those of Bureau of Standards benzoic acid and potassium acid phthalate. The acid equivalent of adipic acid was found by potentiometric titration with a standard base, and the acid content of the glycolic acid solution was determined by oxidation with standard ceric sulfate. Weighed amounts to give the desired concentrations were dissolved in water with the aid of a mechanical shaker before an excess of either reagent-grade calcium carbonate (Baker's) or basic magnesium carbonate (B & A) was added, and they were allowed to stand at room temperature with intermittent shaking until equilibrated. Calcium and magnesium in the liquid phases were determined by EDTA titration. Benzoic, phthalic, and adipic acid were determined by ultraviolet spectrophotometry after removing the interfering calcium and magnesium from the adipate solutions with an ion-exchange column. Glycolic acid was determined volumetrically by the method of Williard and Young [J. Am. Chem. Soc., 52, 132 (1930)]. Solutions were considered to be equilibrated when the calcium or magnesium analysis of succeeding samples taken at least 3 days apart agreed within the limits of the method used. The values shown are averages of the final two determinations. The concentrations of the organic acids found were within analytical variation of the weighed amounts added. The mole ratios M:(-COOH) listed in Table I were obtained by taking the average of the organic acid determined by analysis of the saturated solution and that added to the original solution.

The ratios of metal to -COOH groups of the organic acid, shown in Table I, increased with decreasing amounts of the acid added. This may be caused by the slight solubility of the metal carbonates in water. These ratios are shown in the figure as a function of the weight percent of the acid added to the solution. Magnesium carbonate is dissolved quite efficiently by the organic acid solutions, and calcium carbonate also is dissolved in ratios slightly greater than the stoichiometric value of 0.5 for most of the solutions in this concentration range. The higher pH values of solutions saturated with $MgCO_3$ may be caused by the basicity of the reagent carbonate used as well as the greater solubility of the magnesium compound.

Work done under OAP-TVA Contract No. TV-34425A

April 1971 - FR

TABLE I

Solubility of Calcium and Magnesium Carbonates

in Solutions of Organic Acids at 25°C

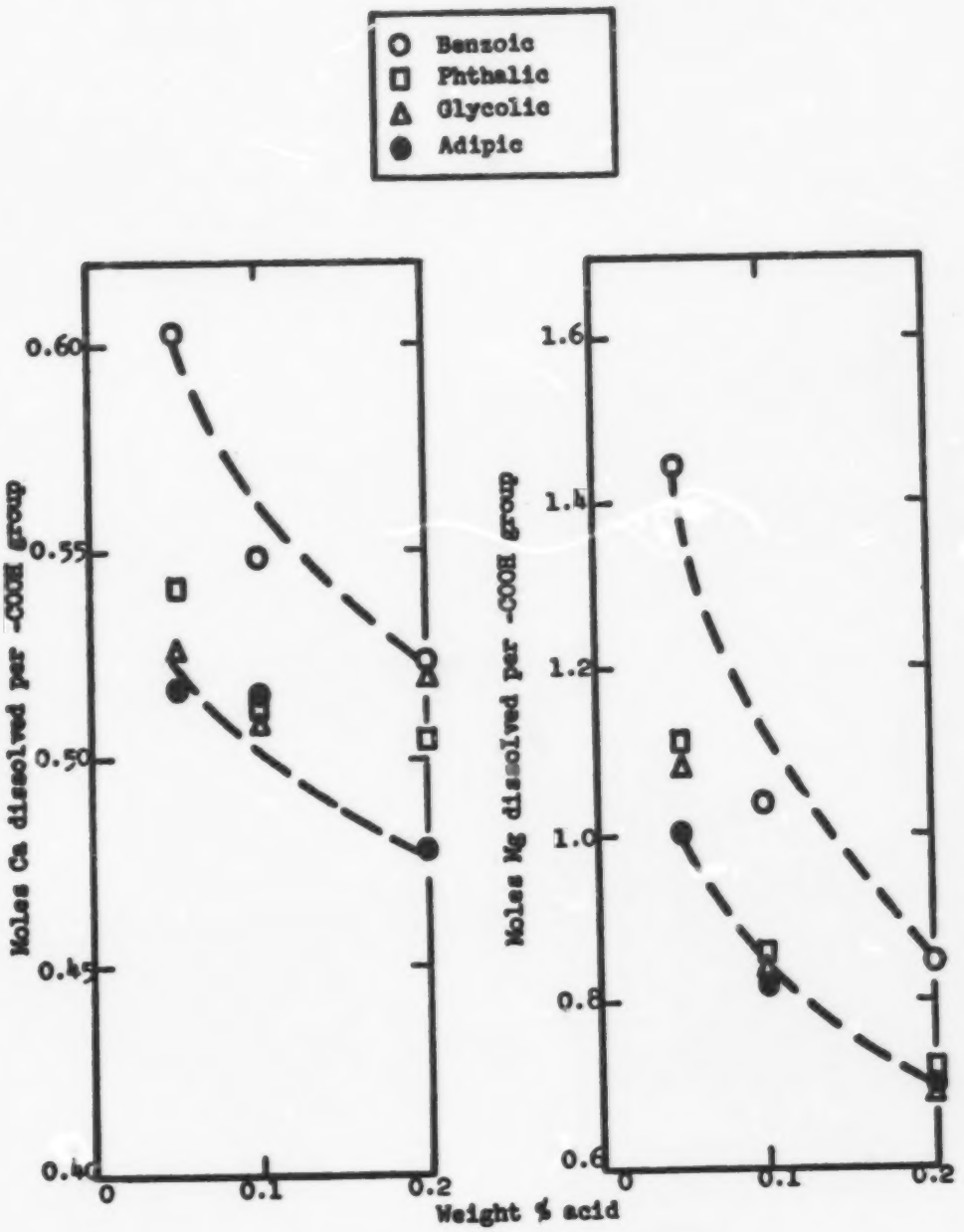
Acid	Wt. % of acid	Satd. $CaCO_3$ solns. pH	Molarity x 10^3 Ca	Molarity x 10^3 Organic acid	Mole ratio Ca:(-COOH)	Satd. $MgCO_3$ solns. pH	Molarity x 10^3 Mg	Molarity x 10^3 Organic acid	Mole ratio Mg:(-COOH)
Benzoic	0.05	8.0	2.42	3.95	0.60	9.4	5.88	4.05	1.45
	0.1	7.9	4.42	8.00	0.55	9.1	8.51	8.20	1.04
	0.2	8.2	8.58	16.4	0.52	8.9	13.7	16.0	0.85
Phthalic	0.05	8.1	3.19	2.88	0.54	9.4	6.53	2.88	1.11
	0.1	8.0	6.08	5.85	0.51	9.1	10.2	5.90	0.86
	0.2	7.9	11.9	11.6	0.50	8.8	17.1	11.8	0.72
Glycolic	0.05	8.1	3.23	3.75	0.53	9.3	7.12	6.60	1.08
	0.1	8.0	6.64	12.9	0.51	9.2	11.3	13.7	0.84
	0.2	7.8	13.8	26.9	0.52	9.0	18.8	28.2	0.69
Adipic	0.05	8.0	3.69	3.73	0.52	9.3	7.17	3.73	1.00
	0.1	7.9	7.15	7.00	0.52	9.1	11.5	7.00	0.83
	0.2	7.8	14.1	16.0	0.48	9.0	19.3	14.0	0.70

TABLE II

Solubility of Calcium and Magnesium Salts

of Organic Acids at 25°C

Salt	Saturated solution pH	Molarity x 10^3 Ca or Mg	Molarity x 10^3 Organic acid
Calcium benzoate	7.4	99.8	196.
Calcium phthalate	6.4	16.1	15.5
Calcium glycolate	7.1	80.4	158.
Calcium adipate	7.6	173.	171.
Magnesium benzoate	9.2	356.	700.



Dissolution of $CaCO_3$ and $MgCO_3$ by

Solutions of Organic Acids at 25°C

The saturation solubility at 25°C of the calcium salts of the four acids and magnesium benzoate is shown in Table II. The purity of all the salts (February report) was checked by wet analysis for calcium or magnesium and all were practically theoretical in composition. Saturation was obtained by placing an excess of the salt in water and allowing it to stand at room temperature with occasional shaking until analysis indicated that the concentration of the liquid phases was constant.

The analytical methods were those used for the dilute solutions in Table I even though ultraviolet spectrophotometry is not as suitable for concentrated solutions because of dilution errors. This could have contributed to the lack of stoichiometry in the mole ratios of metal to acid for the saturated solutions of Table II.

Similar studies at 50°C are in progress. A computer program is being written to calculate the species concentrations of the solutions and to evaluate from the data the association of the metals with the organic acids in solution. (J. D. Hatfield, R. C. Mullins)

Constants Derived From Solubility Measurements

The data reported in April on the solubility of $CaCO_3$ in solutions of the four organic acids being studied (benzoic, glycolic, phthalic, and adipic) were analyzed by a computer program to evaluate the concentration of species in the solutions and to determine the stability constant of the complex, CaA (A = organic anion)

$$CaA \rightleftarrows Ca + A, \quad K_{cpx} = a_{Ca}a_{A}/a_{CaA} \qquad (1)$$

The activity coefficients and equilibrium constants for other equilibria used by Radian Corporation (PB193029) were used in this program.

The densities of the solutions were measured and the original molar concentrations were converted to molalities for the computations. In addition, the pH of each solution was redetermined more accurately to obtain smaller variance of the stability constant, K_{cpx}. The ionization constants of the organic acids with the exception of benzoic were taken from Special Publication No. 17 of The Chemical Society (1964). The ionization constant of benzoic acid was taken from Smolyakov and Primanchuk, [Russ. J. Phys. Chem. 40, No. 3, 331-3 (1966)]; their data agree well with those of other investigators and cover the temperature range 25° to 90°C.

The thermodynamic ionization constants (infinite dilution) are summarized in the tabulation.

Dissociation Constants at 25°C

Acid	K_1	log K_1	K_2	log K_2
Benzoic	$6.24 \cdot 10^{-5}$	-4.205	-	-
Glycolic	$1.48 \cdot 10^{-4}$	-3.831	-	-
Phthalic	$7.25 \cdot 10^{-4}$	-3.14	$4.0 \cdot 10^{-6}$	-5.40
Adipic	$3.8 \cdot 10^{-5}$	-4.42	$3.9 \cdot 10^{-6}$	-5.41

The reported data for the ionization constants of benzoic and glycolic acids with temperature were put in the form used by Radian Corporation.

$$\log K = -A/T - B \log T - CT + D \qquad (2)$$

The coefficients were determined by least squares and their significance was determined by statistical tests. The coefficients are shown in the tabulation.

Acid	A	B	C	D
Benzoic	804.7	0	0.0090476	1.192
Glycolic	1327.1	0	0.0144969	4.942

The ionization constants of dibasic phthalic and adipic acids at temperatures other than 25°C have not been reported.

The calculations were made for the system $CaO\text{-}CO_2\text{-}H_nA\text{-}H_2O$ where A is the acid anion, n = 1 for benzoic and glycolic acid, and n = 2 for phthalic and adipic acids. The solutions were saturated with $CaCO_3$, and the total concentrations of calcium and acid were determined, the acid both by analysis and by weighing the amount of acid added to the total solution. The pH of each solution was determined and equations corresponding to the following equilibria were solved.

$H_2O \rightleftarrows H + OH$
$[H_2A \rightleftarrows HA + A]$
$HA \rightleftarrows H + A$
$CaOH \rightleftarrows Ca + OH$
$CaHCO_3 \rightleftarrows Ca + HCO_3$
$CaCO_3 \rightleftarrows Ca + CO_3$
$H_2CO_3 \rightleftarrows H + HCO_3$
$HCO_3 \rightleftarrows H + CO_3$
$CaA \rightleftarrows Ca + A$
$\Sigma CA = Ca + CaOH + CaHCO_3 + CaCO_3 + CaA$
$\Sigma A = [H_2A] + HA + A + CaA$
$\Sigma CO_2 = CaHCO_3 + CaCO_3 + H_2CO_3 + HCO_3 + CO_3$
$\Sigma Z_i m_i = 0$

Activity coefficients, γ_i, which relate the activity, a_i, and molality, m_i, of each aqueous species, were calculated from the expression

$$\log \gamma_i = A^* Z_i^2 [-I\ 1/2/(1 + B^*{}^{o}_{a_i}\ I\ 1/2) + b_i I] + U_i I \qquad (3)$$

where A* and B* are the temperature-dependent Debye-Hückel terms, and Z_i, $\overset{o}{a}_i$, b_i, and U_i are the valence, ionic size, and two experimentally determined parameters for each i species, respectively. The parameters for the organic species, for which there were no available values, were taken such that equation 3 reduced to the Davies equation. These parameters were $\overset{o}{a}$ = 3.0, b = 0.3, u = 0.0 for all charged species, and u = 0.076 for uncharged species. The ionic strength, I, was calculated from $I = \Sigma Z_i^2 m_i$, and the activity of the water was calculated from the Gibbs-Duhem relation that has been adapted by Radian Corporation for computer evaluation with the above activity coefficient form (Technical Note 200-004-02, 27 May 1970).

Since the solutions were saturated with $CaCO_3$ and the pH was measured, a direct measurement was obtained of the activities of the aqueous species $CaCO_3$ and H^+; this leaves 12 unknowns and 12 equations for the monobasic acids (13 for the dibasic acids), one of which is the complexity constant, K_{cpx}, of equation 1. Table I summarizes the values of solubility, density, and pH of the solutions and the calculated values of the logarithm of the complexity constant, K_{cpx}. Table II is an example of the computer printout for the solution containing 0.2% benzoic acid when the acid was determined by ultraviolet spectrophotometry.

The data in Table I include values for the organic acid content of the solutions determined by analysis, as described in April, and determined from the weighed amounts added to the solutions. The value of K_{cpx} was calculated for each of these acid concentrations as well as for the average of the two. For benzoic acid, the equations were solvable for all solutions, but for the other acids no values of K_{cpx} were obtained for many solutions because some of the species concentrations were calculated to be negative. This indicates the need for more accurate analyses to describe the systems adequately and to evaluate the complexity constants from solubility data. For example, a 1% error in the analysis of banzoic acid caused a change in the value of K_{cpx} of 32%, 47%, and 81% when the acid concentrations were approximately 0.05, 0.1 and 0.2%, respectively. Similarly, an error of 0.03 pH unit caused an error of about 30% in the value of K_{cpx}.

In Table II the symbol M stands for metal, here calcium, TCO_2 is the total carbonate present in solution in moles per kg H_2O, PCO_2 is the partial pressure of CO_2 in atmospheres over the solution, EN is the electroneutrality balance from solving the equations (the sum of positive charges over negative charges), and I is the ionic strength.

TABLE I

Complexity Constants at 25°C in Solutions Saturated With Calcium Carbonate Containing Organic Acids

Acid	Wt., % of acid	pH	Density, g/ml	10^3 molality			log K_{cpx} when acid is		
				Ca	Acid		analyzed	added	averaged
					Anal.	Added			
Benzoic	0.05	8.04	0.9973	2.428	3.963	4.096	-2.27	-1.85	-2.10
	0.1	7.95	0.9975	4.437	8.030	8.197	-2.31	-1.96	-2.16
	0.2	7.81	0.9984	8.615	16.47	16.41	-2.13	-2.22	-2.18
Glycolic	0.05	8.05	0.9978	3.239	5.766	6.578	-2.14	ns	ns
	0.1	7.98	0.9991	6.655	12.93	13.16	ns	ns	ns
	0.2	7.82	1.000	13.84	26.98	26.35	-2.71	ns	-2.53
Phthalic	0.05	8.14	0.9979	3.199	2.888	3.011	-2.82	ns	-2.14
	0.1	8.00	0.9981	6.100	5.869	6.025	-2.26	ns	ns
	0.2	7.87	0.9990	11.94	11.64	12.063	-2.95	ns	ns
Adipic	0.05	8.02	0.9987	3.698	3.738	3.424	ns	-1.59	ns
	0.1	7.92	0.9990	7.167	7.017	6.849	ns	-2.80	-2.00
	0.2	7.81	0.9988	14.16	16.07	13.71	ns	-3.44	ns

ns No solution obtained because some of the species concentration were calculated to be negative.

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TABLE II

Distribution of Species and Other Properties of Saturated Solutions of $CaCO_3$ Containing 0.2% Benzoic Acid at 25°C

SPECIES	ACTIVITY	MOLALITY	ACT. COEFF
H2O			0.99964
H	0.1549E-07	0.1737E-07	0.8918E+00
OH	0.6533E-06	0.7444E-06	0.8776E+00
HA	0.2653E-05	0.2645E-05	0.1003E+01
A	0.1070E-01	0.1219E-01	0.8776E+00
HA	0.3752E-02	0.4275E-02	0.8776E+00
M	0.2584E-02	0.4299E-02	0.6012E+00
MOH	0.3998E-07	0.4555E-07	0.8776E+00
MHCO3	0.2931E-04	0.3339E-04	0.8776E+00
MCO3	0.7732E-05	0.7709E-05	0.1003E+01
H2CO3	0.2170E-04	0.2164E-04	0.1003E+01
HCO3	0.6237E-03	0.7097E-03	0.8788E+00
CO3	0.1885E-05	0.3161E-05	0.5964E+00

TCOP=	0.7756E-03	PCO2=	0.6342E-03	EN=	0.1325E-09
KCPX=	0.7368E-02	LOGKCPX=	-2.13263	I=	0.17208E-01

DISTRIBUTION

METAL		ACID		CARBONATE	
HA	49.63	HA	0.02	MHCO3	4.31
M	49.90	A	74.02	MCO3	0.99
MOH	0.00	HA	25.96	H2CO3	2.79
MHCO3	0.39			HCO3	91.50
MCO3	0.09			CO3	0.41

Table III is a summary of the calculated distributions of calcium and acid between ionic and complex forms in the solutions. Small amounts of other species are present, but 99% or more of both calcium and acid at these pH's exists as the complex, CaA, and the free ion, Ca^{2+} or A^- (A^{2-} for dibasic acids). The data for benzoic acid are quite reliable because of the high precision of the analysis and the relative constancy of K_{cpx} at different concentrations of acid. The fraction of calcium or acid in the complex form increases as the acid concentration is increased. The data for glycolic, phthalic, and particularly adipic acids are less reliable and only indicate a trend; little significance should be assigned to the magnitude of the distribution.

A similar study was made for the solutions saturated with $MgCO_3$ (April report), but the solution of the equations resulted in some negative concentrations of aqueous species. This indicates that either the analyses of the solutions are not sufficiently accurate, the model is incorrect, or the constants for the magnesium system equilibria are in error (as has been suspected).

TABLE III

Calculated Distributions of Calcium and Acid Between Ionic and Complex Forms in Saturated $CaCO_3$ Solutions Containing Organic Acids

Acid	Wt. % of acid	Distribution of Calcium		Distribution of Acid	
		M	MA	A	MA
Benzoic	0.05	75	24	86	14
	0.1	61	38	79	20
	0.2	50	50	74	26
Glycolic	0.05	31	68	83	17
	0.1	-	-	-	-
	0.2	24	76	61	39
Phthalic	0.05	86	13	86	14
	0.1	78	22	77	23
	0.2	41	59	40	60
Adipic	0.05	94	5	95	5
	0.1	54	46	52	48
	0.2	24	76	21	79

(J. D. Hatfield, R. C. Mullins, R. L. Dunn)

Solubilities of Salts of Organic Acids at 50°C: The results of measurements of the solubilities at 50°C of the calcium and magnesium salts of the four organic acids--benzoic, phthalic, adipic, and glycolic--are shown in Table I, together with the solubilities at 25°C that were reported in April. Stoichiometric mixtures of each acid with calcium or magnesium carbonate were shaken intermittently in water at 50.0° ± 0.1°C until the compositions of the liquid phases became constant. Saturated solutions were prepared similarly from the calcium salts of the acids also. Except for the glycolate, the results obtained by the two methods for the calcium salts were the same within experimental error.

Microscopic examination showed that the solid phases in the benzoate, phthalate, or adipate mixtures prepared from the carbonate were the same as those prepared from the reagent salts. The solid phase in the solution made from calcium carbonate and glycolic acid was predominately $2(CH_2OHCO)_2Ca \cdot 3H_2O$, whereas that in the solution prepared from anhydrous calcium glycolate was anhydrous. The difference in composition of the glycolate solutions therefore represents the difference in solubility of the trihydrate and the anhydrous salt. The pH of the solutions prepared from the carbonates and the acids, however, were consistently lower than those prepared from the salts, presumably because they were saturated with CO_2.

The solubility of the salts of the monobasic acids--benzoic and glycolic--increased with rising temperature and those of the dibasic acids--phthalic and adipic--decreased. The relative insolubility of calcium phthalate is noteworthy.

As shown in Table II, the solubilities at 50°C of calcium and magnesium carbonates in 0.1% solutions of the organic acids are the same within experimental error as those at 25°C (April report). The concentration of acid is the limiting factor, and temperature, up to 50°C, has no effect on the solubility. The pH's of the solutions at 50°C were significantly lower than those at 25°C; the reason for this effect is not apparent.

TABLE I

Solubility of Calcium and Magnesium Salts of Organic Acids

Acid	Satd. soln. at 70°C pH	Satd. soln. at 70°C Concn., M, x 10^2 Ca or Mg	Satd. soln. at 70°C Concn., M, x 10^2 Acid anion	Satd. soln. at 25°C[a] pH	Satd. soln. at 25°C[a] Concn., M, x 10^2 Ca or Mg	Satd. soln. at 25°C[a] Concn., M, x 10^2 Acid anion
Calcium salts						
Benzoic						
Acid + $CaCO_3$	5.8	13.6	27.4	-	-	-
Reagent salt	6.8	13.6	26.8	7.4	10.0	19.6
Phthalic						
Acid + $CaCO_3$	7.1	1.21	1.15	-	-	-
Reagent salt	7.4	1.22	1.18	6.4	1.61	1.55
Adipic						
Acid + $CaCO_3$	6.2	11.0	11.3	-	-	-
Reagent salt	7.6	10.7	10.9	7.6	17.3	17.1
Glycolic						
Acid + $CaCO_3$	5.5	21.4	42.8	-	-	-
Reagent salt	6.7	17.1	34.3	7.1	8.0	15.8
Magnesium salts						
Benzoic	5.2	89.4	179.	9.2	35.6	70.0
Phthalic	6.6	179.	183.	-	-	-
Adipic	5.9	142.	148.	-	-	-
Glycolic	4.9	71.5	146.	-	-	-

[a] Data reported in April 1971.

TABLE II

Solubility of Calcium and Magnesium Carbonates in 0.1% Solutions of Organic Acids

Acid	Satd. soln. at 50°C				Satd. soln. at 25°C[a]			
	pH	Concn., M, x 10^3 Ca or Mg	Concn., M, x 10^3 Acid anion	Mole ratio metal: anion	pH	Concn., M, x 10^3 Ca or Mg	Concn., M, x 10^3 Acid anion	Mole ratio metal: anion
Calcium salts								
Benzoic	7.2	4.44	8.08	0.55	7.9	4.42	8.00	0.55
Phthalic	6.8	6.19	5.94	1.04	8.0	6.08	5.85	1.02
Adipic	6.8	7.80	7.19	1.08	7.9	7.15	7.00	1.02
Glycolic	6.7	8.71	16.5	0.53	8.0	6.64	12.9	0.51
Magnesium salts								
Benzoic	8.3	8.05	8.31	0.97	9.1	8.51	8.20	1.04
Phthalic	8.4	10.7	6.09	1.75	9.1	10.2	5.90	1.72
Adipic	8.3	11.9	6.95	1.71	9.1	11.5	7.00	1.66
Glycolic	8.2	12.2	15.1	0.81	9.2	11.3	13.7	0.84

[a] Data reported in April 1971.

The calcium and magnesium contents of the 50°C solutions were determined by EDTA titration, and the organic acid contents were determined by potentiometric titration of eluates from passage of the solutions through a cation resin column. The eluates were heated to boiling to remove CO_2 and cooled before the titrations.

Attempts to calculate stability constants for assumed aqueous complexes from the solubility data at 50°C were unsuccessful for the glycolates and phthalates because the calculations gave negative concentrations of some species. For the benzoate and adipate solutions containing calcium carbonate the data are consistent with the following equilibria at zero ionic strength.

$$CaBz^{+} \rightleftarrows Ca^{++} + Bz^{-} \qquad K_{cpx} = 0.1$$

$$CaAd \rightleftarrows Ca^{++} + Ad^{--} \qquad K_{cpx} = 0.003$$

Bunting and Thong [Can. J. Chem. 48, 1654 (1970)] reported a value of 0.63 for the ionization constant of $CaBz^{+}$ at 30° and an ionic strength, I, of 0.4. From the Davies expressions for activity coefficients, the thermodynamic ionization constant (I = 0) of $CaBz^{+}$ at 30°C is calculated from Bunting's data to be 0.16 as compared with our measured value of 0.1 at 50°C. No comparable data were found for the adipate.

COMPLEXES IN SOLUTION

This report describes studies of the chemical composition of solutions containing calcium and benzoic acid. The literature contains no information on the formation of complexes of calcium benzoate, such as $CaBz^+$ or $CaBz_2$, as aqueous species; this information is needed to help define the chemistry of reactions occurring in wet-limestone scrubbing in the presence of organic additives. The method of continuous variation, Job's method [Ann. Chim. [10] 9, 113 (1928)], was used to treat data obtained with the calcium ion selective electrode (Beckman) and the Cary 17 ultraviolet spectrometer.

Calcium Ion Electrode Studies: Calcium perchlorate tetrahydrate, $Ca(ClO_4)_2 \cdot 4H_2O$, was prepared from reagent grade $CaCO_3$ and 70% $HClO_4$. A slight excess of freshly calcined $CaCO_3$ was added to the acid, the mixture was filtered, and the filtrate was concentrated by evaporation. The crystals that separated on cooling were filtered off and dried in a desiccator. A stock solution of the crystals was analyzed for calcium, and portions of the solution were diluted for electrode calibration and testing.

Sodium benzoate (U.S.P.) was purified by recrystallization. The crystals, dried at 105°C, analyzed 15.91% Na (theory 15.96) and were used for preparing a stock solution for dilution.

The calcium ion electrode was calibrated immediately prior to making the measurements for complexation. The calibration from 10^{-1} to 10^{-5} molar calcium is shown in Figure 1 in terms of both concentration and activity of the calcium ion. The activity coefficients, $\gamma_{Ca^{2+}}$, were calculated from the extended Debye-Huckel equation used by Radian Corporation [Final report for NAPCA Contract No. CPA-22-69-138, Vol. 1, June 9, 1970] by the expression

$$\log \gamma_{Ca^{2+}} = 4A \left[-I^{1/2}/(1 + 4.5\ B\ I^{1/2}) + 0.1\ I\right] \qquad (1)$$

where A and B are the theoretical Debye-Huckel constants (0.5116 and 0.3292, respectively, at 25°C), and I is the ionic strength ($I = 1/2 \sum_i Z_i^2 C_i$, with Z_i the valence and C_i the concentration of the ith ion). The calibration measurements that spanned the range to be used in the complexation measurements, 10^{-3} to 10^{-4} M, were run in duplicate. The least-squares equation between 10^{-1} and 10^{-4} M,

$$\log A_{Ca} = -3.0636 + 0.03328E \qquad (2)$$

corresponds to a slope of 30.0 mv/decade (theoretical 29.6) and represents the activity of the calcium ion with a standard deviation of 2%. This variability agrees with the duplicate measurements and is perhaps due to the slow response time of the electrode, and the influence of the immediate past history of the electrode (memory effect). The procedure in determining the "equilibrium" emf of the cell

calcium electrode/solution containing Ca^{2+}/standard calomel electrode

was to record the readings at 1-minute intervals until two successive readings were identical to tenths of a millivolt; this sometimes required more than 10 minutes and a slow drift may have continued much longer--depending on the solution in which the electrode had been immersed in the previous measurement.

A series of samples was prepared by mixing 10^{-3}M $Ca(ClO_4)_2$ with 10^{-3}M C_6H_5COONa in the volume ratios indicated in Table I. The volume of each sample was 100 ml, and the concentrations of calcium and benzoate varied in regular order as shown in columns 3 and 4 of Table I. Concentrations between 10^{-3} and 10^{-4}M were chosen to minimize the effect of ionic strength on the activity coefficients and of Na^+ on the electrode. The millivolt readings in column 5 of Table I were converted to activities of the calcium ion by use of equation 2, and the results are given in column 6; the pH values of the mixtures are shown in column 7.

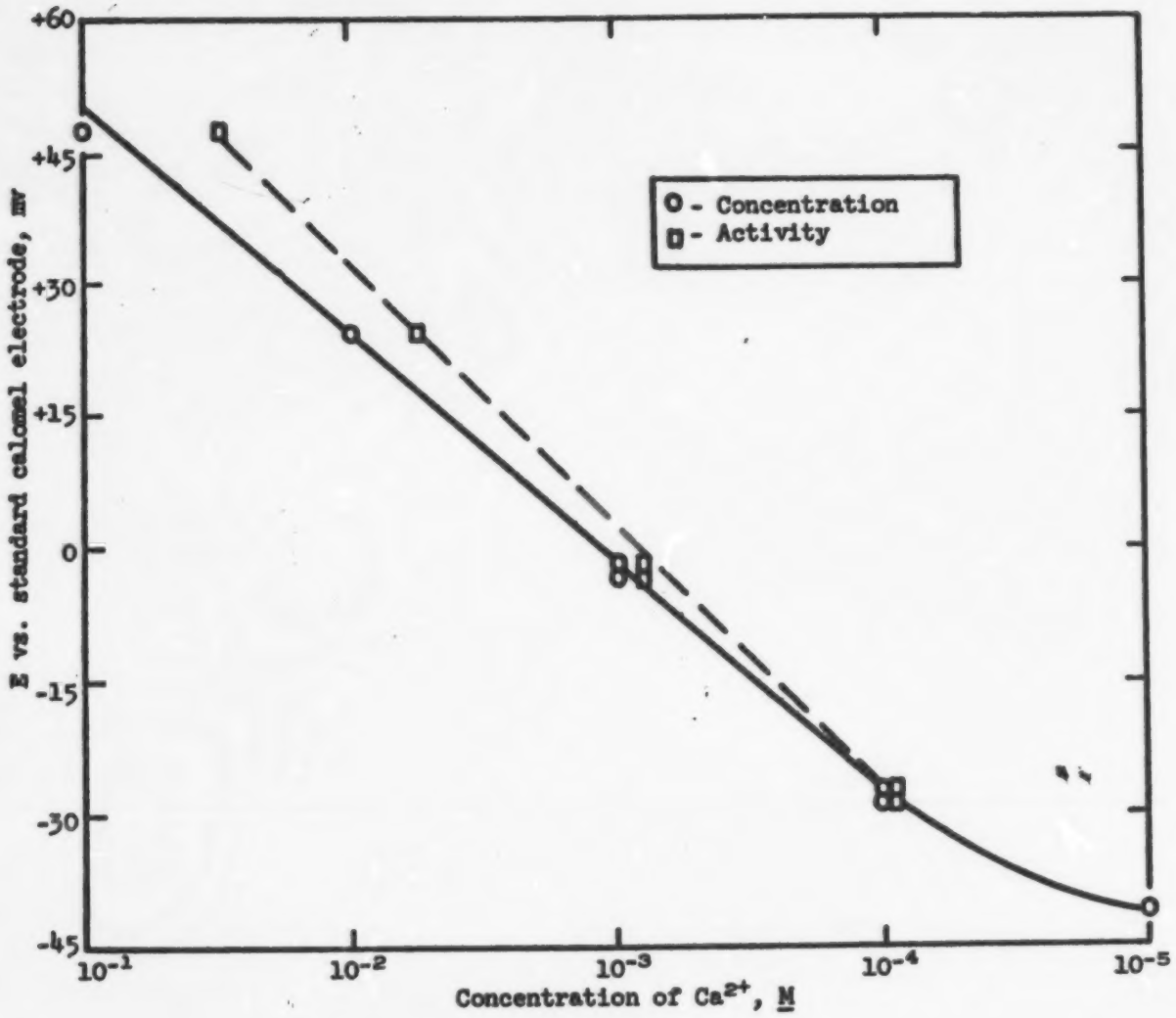


Figure 1

Standardization of Calcium Ion Selective Electrode

[Calcium supplied by standard $Ca(ClO_4)_2$ solutions]

TABLE I

Study of Calcium Benzoate Complex at 25°C

Soln. composition, ml 1×10^{-2} M $Ca(ClO_4)_2$	1×10^{-3} M C_6H_5COONa	Total calcium, M x 10^4	Total benzoate, M x 10^4	Emf, Ca electrode vs. standard electrode, mv	Ca activity, M x 10^4 (from eq. 2)	pH
0	100	0	10.0	-	-	6.30
10	90	1.0	9.0	-25.6	1.2	6.32
20	80	2.0	8.0	-20.3	1.8	6.29
30	70	3.0	7.0	-17.1	2.3	6.37
40	60	4.0	6.0	-15.5	2.6	6.35
50	50	5.0	5.0	-12.1	3.4	6.29
60	40	6.0	4.0	-10.6	3.8	6.34
70	30	7.0	3.0	-7.0	5.1	6.26
80	20	8.0	2.0	-5.2	5.8	6.39
90	10	9.0	1.0	-4.2	6.3	6.29
100	0	10.0	0	-2.0[a]	7.4	6.17

[a] Calibration reading.

Figure 2 shows the relation between the activity of the calcium ion, $A_{Ca^{2+}}$, and the total calcium in solution. Some of the variation in the data can be attributed to the performance of the electrode, and some of the variation may be attributed to the effect of atmospheric CO_2 on the system over which there was no control. There were no sharp breaks in the relation to indicate a definite complex as $CaBz^+$ or $CaBz_2^0$ (Bz = benzoate ion, $C_6H_5COO^-$). While the measured activity of calcium ion was only 70 to 80% of that expected if completely ionized (dotted line, Figure 2), the difference is more than likely due to complexes such as $CaOH^+$ and $CaCO_3^0$ that are known to exist. The variability of pH would indicate differences in the amount of CO_2 absorbed by the solutions and would preclude the use of these measurements in calculating the strength of any possible calcium benzoate complex.

Ultraviolet Absorption Studies: The characteristic absorption peaks for solutions of benzoic acid or sodium benzoate are located at 193 μm and 227 μm, and the absorbances at these wave lengths obey Beer's law (July report). Freshly prepared solutions with the same compositions as those used for the calcium electrode measurements were used to study the effect on the absorbances in a 1-mm cell. The results are shown in Figure 3. There is a linear increase in the absorbances with increase in total benzoate, and there are no breaks in the absorbances. There were also no new absorbance bands as would be expected if a new species were formed by adding calcium. It is possible that a new calcium benzoate species forms that absorbs at the same wave lengths as does benzoic acid, but this is very unlikely.

The results of the ultraviolet absorption and the calcium ion electrode both indicate that no complex between calcium ion and benzoate ion that can be measured by these methods is formed in solution. If such a complex is formed it is very weak, and calcium benzoate solutions can be considered completely ionized--other than the effects of hydrolysis of the ions and reactions with other components of the solution.

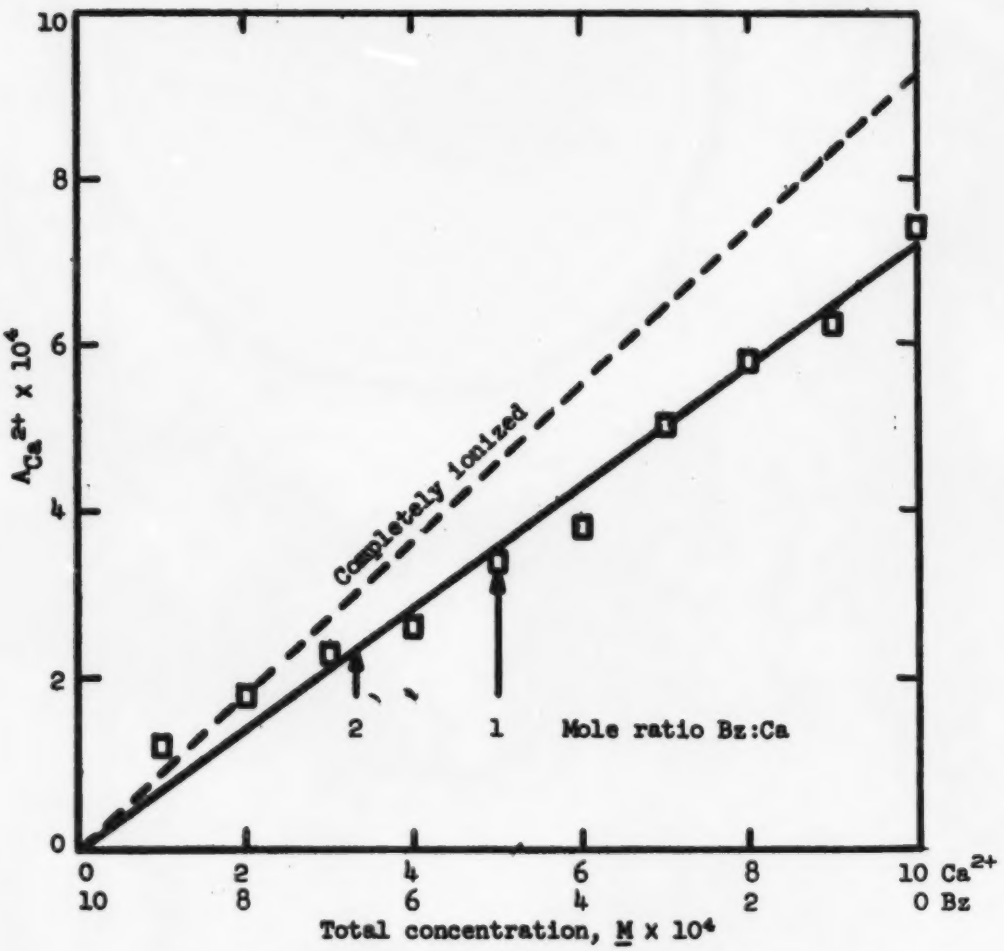


Figure 2

Activity of Calcium in Calcium

Perchlorate-Sodium Benzoate Solutions

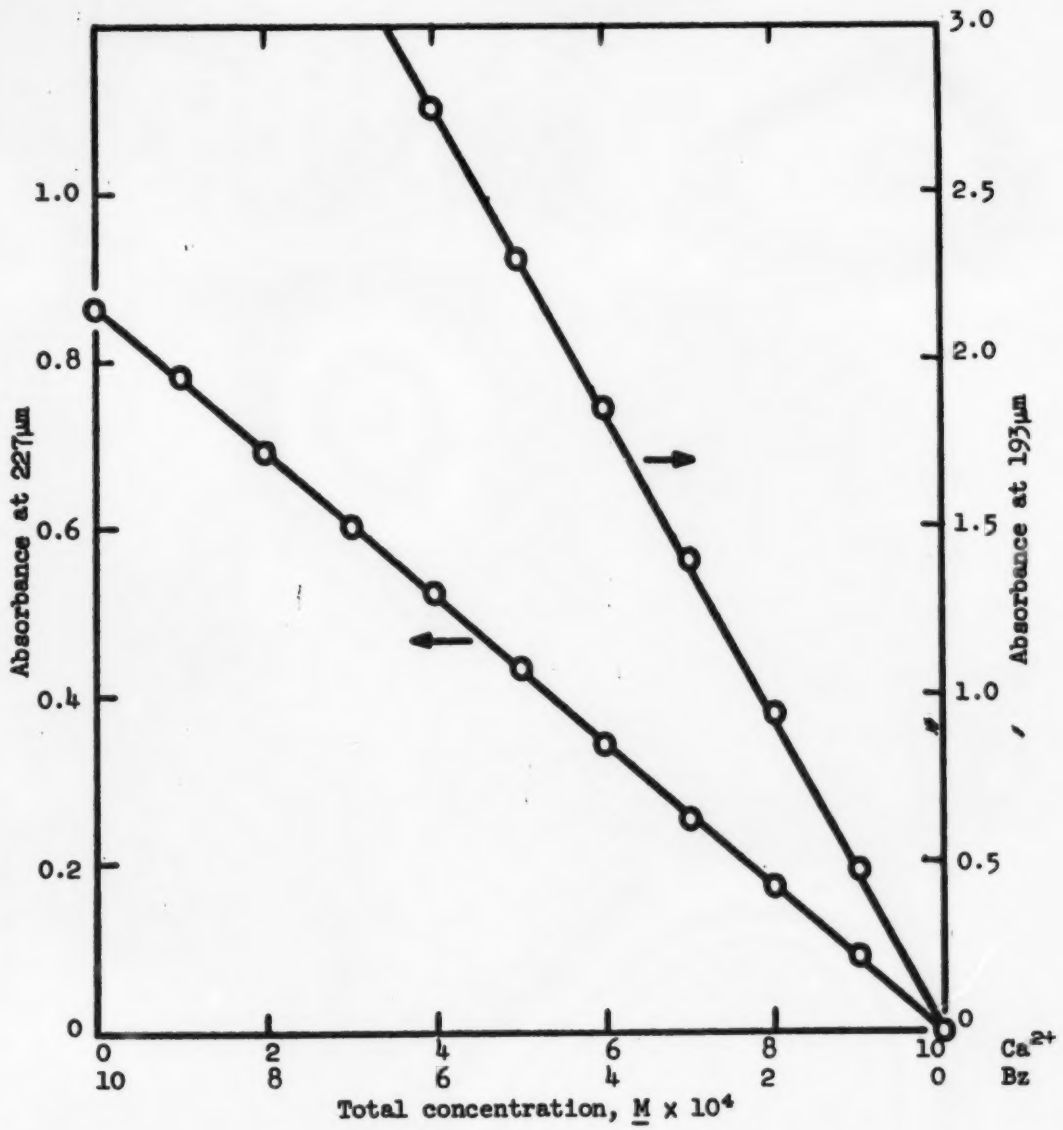


Figure 3

Ultraviolet Absorbance of Calcium

Perclorate-Sodium Benzoate Solutions

December 1970 - FR

Spectroscopic Study of Calcium Benzoate Complexes: Information on the formation of complexes is needed in understanding the behavior of organic additives in the wet-limestone scrubbing of SO_2. Benzoic acid solutions absorb at 275 and 192 nm in the ultraviolet region (July 1970 report); the peaks are sharp and Beer's law is obeyed in the concentration range 10^{-3} to 10^{-4} molar. A calcium benzoate complex formed in aqueous solution probably would have different absorption characteristics, and infrared spectroscopy should be useful in identifying this complex. In exploratory tests (December 1970 report) no complex was detected, but it was found that the pH of the benzoate solutions affects the absorbance. In further studies the pH was adjusted to either 5 or 8 by addition of tetramethylammonium hydroxide to solutions of calcium perchlorate and benzoic acid before measuring the absorbance. The results are given in Table IV. Neither perchlorate nor tetramethylammonium ions absorb appreciably under the experimental conditions and do not form complexes. Tests at pH 5 and 8 showed that the absorbance is proportional to the benzoic acid concentration when the calcium concentration is constant and that the absorbance is constant when the calcium concentration is varied. These results indicate that any aqueous calcium benzoate complex formed is so weak that it does not affect the absorbance of the normal benzoate species in solution. This is in agreement with results of previous studies with the ion-selective electrode (December 1970 report) that indicated that calcium benzoate solutions could be considered almost completely ionized. The ionization constant calculated from the solubility data at 50°C (K_{cpx} = 0.1) indicates that less than 1% of the benzoate in solution is complexed as $CaBz^+$ when the calcium ion concentration is in the range shown in Table IV. This complex is too weak to affect ultraviolet absorbance measurements, and the ion-selective electrode does not detect such small changes in concentration.

TABLE IV

Ultraviolet Absorbance of Calcium Benzoate Solution at Room Temperature (25°-27°C)

Composition, M x 10^4, of solution			Absorbance at indicated wavelength, nm	
$Ca(ClO_4)_2$	C_6H_5COOH	$N(CH_3)_4OH$	225	192
Measurements at pH 5.0				
2	1	0.96	0.074	0.40
	2	1.9	0.159	0.85
	3	2.7	0.243	1.30
	4	3.6	0.325	1.72
	5	4.5	0.405	2.16
1.6	4	3.6	0.324	1.71
1.2	4	3.6	0.323	1.70
0.8	4	3.6	0.324	1.71
0.4	4	3.6	0.324	1.71
0.0	4	3.6	0.323	1.70
Measurements at pH 8.0				
2	1	1.7	0.086	0.46
	2	2.8	0.173	0.92
	3	3.2	0.255	1.37
	4	4.2	0.342	1.84
	5	5.2	0.432	2.30
1.6	4	4.3	0.431	1.83
1.2	4	4.3	0.431	1.82
0.8	4	4.3	0.432	1.82
0.4	4	4.3	0.431	1.83
0.0	4	4.3	0.431	1.82

VOLATILITY OF ORGANIC ACIDS UNDER SCRUBBING CONDITIONS

Vapor Pressure of Benzoic Acid in Water: The partial pressure of benzoic acid over its aqueous solution was measured by a dynamic method similar to that described by Johnstone [Ind. Eng. Chem. 27, 587 (1935)]. Nitrogen gas was saturated by passage through a solution of 1.6 grams of benzoic acid per liter, and the exit gas was scrubbed with a Vanier-type bulb on the exit tube. The benzoic acid in the scrubbing bulb was determined by diluting the sample with deionized water and measuring the ultraviolet absorbance of the solution.

It was found that the vapors of benzoic acid were absorbed by both the neoprene stopper and the stopcock grease in the joints of the apparatus. The stopcock grease was eliminated from the apparatus, and after many determinations the neoprene stopper in the top of the saturation vessel apparently became equilibrated or perhaps saturated with the benzoic acid. Reproducible results then were obtained in duplicate runs.

The partial pressures of benzoic acid over a solution containing 1.6 grams/liter were measured at three temperatures with the following results:

Temp., °C	Partial pressure of benzoic acid atm, x 10^5
40	1.336
55	2.07
65	2.79

From the temperature dependence of the ionization constant, K_1, of benzoic acid [Russian J. of Phys. Chem. 40, 331 (1966)]

$$\log K_1 = -804.7/T - 0.0090476T + 1.192 \qquad (1)$$

and the activity coefficients used by Radian Corporation [Final report, NAPCA Contract No. CPA-22-69-138, Vol. 1, June 9, 1970], the degree of dissociation at each temperature was calculated, and from this the activity of undissociated benzoic acid, A_{HBz}, and the Henry's law constant, h, were calculated.

$$h = P_{HBz}/A_{HBz} \qquad (2)$$

The results are shown in the tabulation.

Temp., °C	h, atm/molality
40	1.088×10^{-3}
55	1.684×10^{-3}
65	2.266×10^{-3}

Both the partial pressure of benzoic acid, P_{HBz}, and the Henry's law constant, h, were related to the absolute temperature, T, by equations determined by the method of least squares.

$$\log P_{HBz} = -0.5662 - 1349.4/T \qquad (3)$$

and

$$\log h = 1.3285 - 1344.6/T \qquad (4)$$

Equation 3 applies only to the concentration of benzoic acid used (1.6 grams/liter) and implies a heat of vaporization of 6,200 cal/mole from solution as compared with a sublimation energy of 21,900 cal/mole for the pure acid. Equation 4 and equation 2 may be used to calculate the vapor pressure at any temperature and concentration at which A_{HBz} can be determined or calculated.

The vapor pressure of benzoic acid over scrubbing solutions in the pH range 4 to 7 were estimated from the relation

$$\log(A_{HBz}/A_{Bz}) = pK_1 - pH \qquad (5)$$

where A_{Bz} is the activity of the benzoate ion and the symbol p indicates the negative logarithm. If it is assumed that the activity coefficients for the benzoate species are unity, the following vapor pressures at 55°C are calculated for a total benzoate concentration of 0.01 m (about 1.2 grams/liter).

pH	P_{HBz}, ppm (volume basis)
4	11.0
5	2.4
6	0.28
7	0.028

The vapor pressures of benzoic acid solutions in the pH range 4 to 7 is too low to measure in our laboratory equipment, but values estimated from the consistent data obtained thus far probably are correct within an order of magnitude. This range of vapor pressures is a serious consideration in scrubbing operations, since a vapor pressure of 1 ppm over solutions used to scrub the gas from a 500-megawatt boiler would produce more than 40 liters per minute (>200 grams) of benzoic acid vapor in the exit flue gas.

The above results will be checked with an apparatus fabricated with Teflon seals. The vapor pressures of solutions of phthalic, glycolic, and adipic acids will be determined also. (J. D. Hatfield, Y. K. Kim, R. C. Mullins, M. E. Deming)

January 1971 - FR

Vapor Pressure of Benzoic Acid Solutions: The partial pressure of benzoic acid at 3 temperatures was reported in January for a concentration of 1.6 grams benzoic acid per liter. The data reported were consistent with the integrated Clausius-Clapeyron equation, but they implied a heat of vaporization of 6.2 kcal/mole as compared with a value of 21.9 kcal/mole for sublimation. Experimental difficulties of absorption of benzoic acid vapors on the apparatus and on the stopcock grease used at the joints cast doubt on the validity of the results.

September 1971 - FR

The study was repeated in a 4-stage saturator with the sidearm heated about 10°C above that of the run temperature. The grease-free joints were flamed briefly at the end of a run to remove absorbed vapors. After conditioning the apparatus by many runs to a quasi-steady state, consistent results were obtained, as shown in the figure. The data are expressed by the relation

$$\log P_{atm} = 9.20 - 4,787/T$$

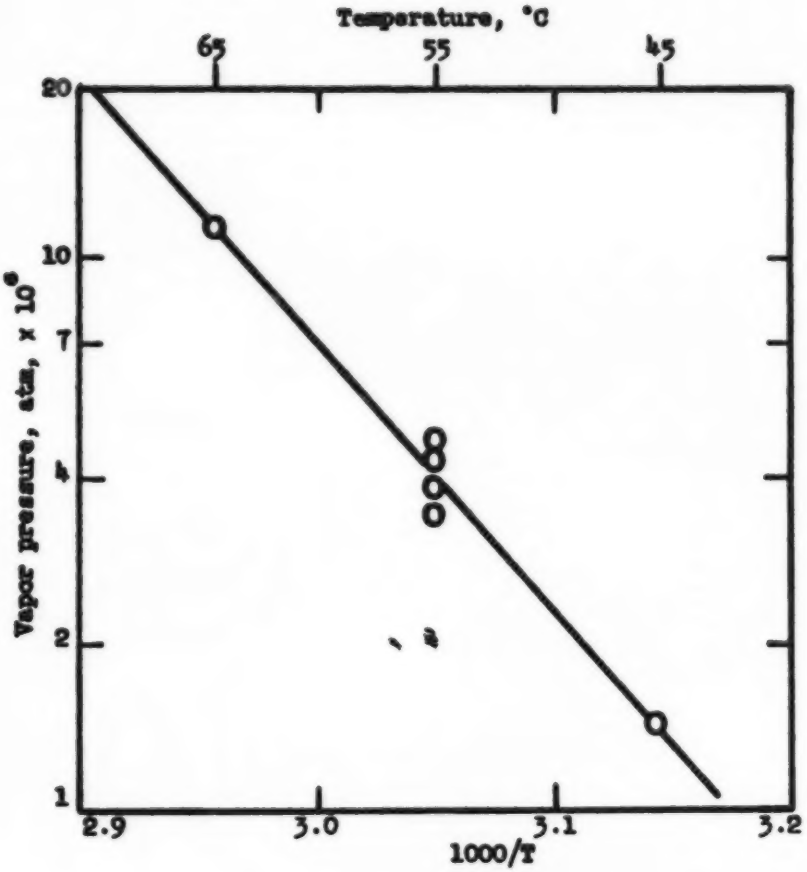
which indicates an energy of vaporization of 22 kcal/mole. In January the Henry's law constant for evaporation was used, and its reciprocal is used here to conform to the convention used by the Radian Corporation in their computer program described in PB193029. The Henry's law constant, h, for absorption then becomes

$$\log h = -10.27 + 4500/T$$

and the vapor pressures of 0.01 molar benzoate solution at different temperatures and pH are shown in the tabulation.

	Vapor pressure of benzoic acid, ppb, at indicated temperatures		
pH	45°C (113°F)	50°C (122°F)	55°C (131°F)
2	136	217	355
3	129	206	337
4	85	137	225
5	19	31	52
6	2	4	6
7	0.2	0.4	0.6

These data indicate that the losses of benzoic acid under scrubbing conditions will be relatively low. A vapor pressure of 100 ppb would result in the loss of about 2.5 pounds of benzoic acid per hour if the acid were used in the limestone slurry to scrub the gas from a 500-megawatt boiler. It is probable, however, that greater losses would result from absorption on scrubber solids, on surfaces of the equipment, and in the mist from the mist eliminator at the top of the scrubber.



Vapor Pressure of Benzoic Acid

Over Its 0.013 M Aqueous Solution

(1.6 grams C_6H_5COOH per liter)

(J. D. Hatfield, Y. K. Kim,
R. C. Mullins, M. E. Deming,
R. L. Dunn)

EFFECT OF ORGANIC ACIDS ON OXIDATION OF SULFITE

Oxidation of Sodium Sulfite

The addition of an organic acid to limestone slurries to promote SO_2 absorption may also affect the rate of oxidation of sulfite to sulfate in the scrubber. Initial results in the Applied Research pilot unit indicated a considerable increase in the oxidation to sulfate (May 1970). Since the oxidation rate is probably dependent on pH, and the pH changes with the degree of oxidation, a study was made of the effects of the four organic acids (benzoic, phthalic, glycolic, and adipic) in the sodium system in which considerable sulfite can be held in solution to offset rapid pH changes and lengthen the time before oxidation is complete. Similar studies will be made in the calcium system.

The reaction solution was prepared by dissolving reagent-grade Na_2SO_3 and $Na_2S_2O_5$ in the mole ratio 2:3 (mole ratio S:Na = 0.8), and the final concentrations of the Na and S were 2.12 and 1.69 molal, respectively. About 8 to 11% of the total sulfur was in the sulfate form before the run was started because of the oxidation of the chemical in storage and during the preparation of the sample. In each run, 500 ml of the solution was placed in a 1-liter gas-absorption tube equipped with a coarse fritted-glass gas disperser, and the vessel was placed in a water bath at 55°C. Pure oxygen was passed through the glass frit at the rate of 400 cc per minute, and a 25-ml sample was withdrawn every hour for analysis. Immediately after sampling, the total sulfite was determined by iodine titration and the pH was measured; the total sulfur and sodium contents then were determined. The losses of water and SO_2 by evaporation in the large flow of oxygen were determined by the increases in sodium concentration and by the ratio of total sulfur to sodium (assuming no losses of sodium or sulfate); these losses were checked by a computer calculation of the vapor pressures of H_2O and SO_2 and numerically integrating between samples. Results of a typical run are shown in Figure 1; the SO_2 evaporation losses determined by chemical analysis usually agreed fairly well with those determined by vapor pressures but they differed most in the range in which the pH of the solution changed most rapidly. Since the oxidation of sulfite to sulfate lowered the pH, the vapor pressure of SO_2 increased. Therefore, the evaporative loss of sulfite as SO_2 started after about 1 hour and gradually increased until oxidation was essentially complete.

Small amounts of each of the four organic acids were added to similar solutions to study their effects on the oxidation rate; equivalent amounts of NaOH to neutralize the acid were added so that all the starting solutions had the same pH (5.9 ± 0.05) and the same total sulfur concentration. The results are shown in the table.

Work done under OAP-TVA Contract No. TV-34425A

May 1971 - FR

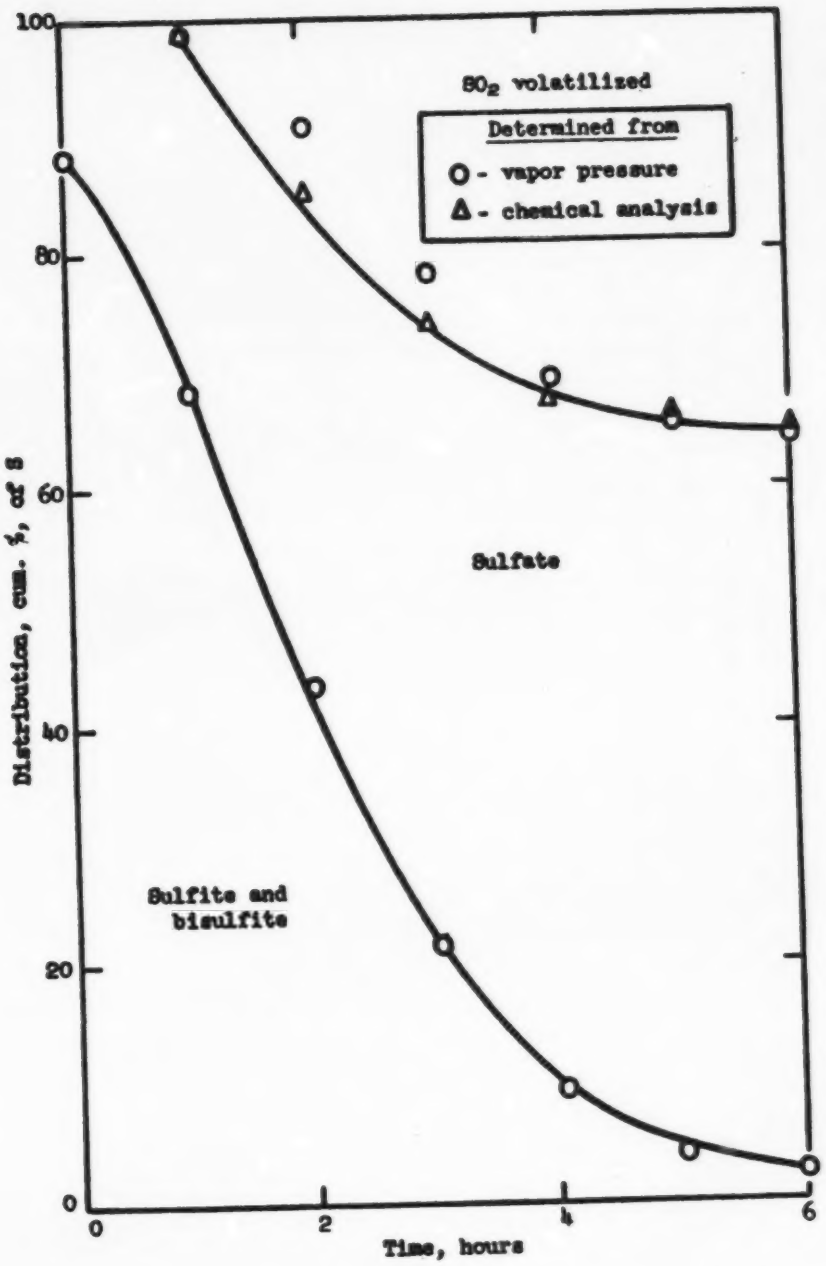


Figure 1

Oxidation of Sulfite to Sulfate in the Sodium System at 55°C

Work done under OAP-TVA Contract No. TV-34425A

May 1971 - FR

Effect of Organic Acids on the Rate of Oxidation at 55°C in the Sodium Sulfite-Bisulfite System

Acid	Concn., %	Time, hr.	pH	Distribution, %, of S		
				Sulfite + bisulfite	Sulfate	SO_2 volatilized
None	--	0	5.88	88.8	11.2	0.0
		1	3.78	68.7	30.3	1.0
		2	3.10	43.8	41.3	14.9
		3	2.90	21.6	52.6	25.8
		4	2.85	9.6	57.8	32.6
		5	3.03	4.0	62.3	33.7
		6	3.10	2.6	61.6	35.8
Benzoic	0.3	0	5.85	91.7	8.3	0.0
		1	3.12	59.4	33.6	7.0
		2	2.85	22.3	53.0	24.7
		3	2.93	7.7	61.3	31.0
		4	3.32	4.5	62.5	33.0
		5	3.45	2.9	63.5	33.6
		6	3.48	2.3	63.5	34.2
Phthalic	0.3	0	5.87	90.2	9.8	0.0
		1	4.00	67.9	29.6	2.5
		2	3.08	40.1	45.1	14.8
		3	2.77	13.3	58.9	27.8
		4	3.00	5.9	63.1	31.0
		5	3.15	3.6	64.4	32.0
		6	3.35	2.5	65.5	32.0
Glycolic	1.0	0	5.92	91.2	8.8	0.0
		1	4.28	69.3	29.5	1.2
		2	3.45	51.0	40.3	8.7
		3	3.23	30.8	51.7	17.5
		4	3.10	14.5	59.8	25.7
		5	3.05	6.5	64.5	29.0
		6	3.28	3.7	66.1	30.2
		7	3.32	2.5	66.5	31.0
Adipic	1.0	0	5.90	90.2	9.8	0.0
		1	4.50	64.5	32.5	3.0
		2	2.88	31.0	52.0	17.0
		3	2.75	9.0	62.8	28.2
		4	3.10	4.5	66.1	29.4
		5	3.35	3.0	66.4	30.6
		6	3.45	2.1	67.3	30.6

Work done under OAP-TVA Contract No. TV-34425A

May 1971 - FR

With each organic acid the oxidation was almost complete in 6 hours, and the pH change and SO_2 evaporative loss pattern were similar for all runs. The effects of the organic acids on the rate of oxidation of sulfite are shown in Figure 2; the data indicate that all the organic acids promoted oxidation in the sodium sulfite-bisulfite system in the order benzoic > adipic > phthalic > glycolic > no acid.

Similar measurements are being made of the rate of oxidation of sulfite in the calcium sulfite-bisulfite system.

Work done under OAP-TVA Contract No. TV-34425A

May 1971 - FR

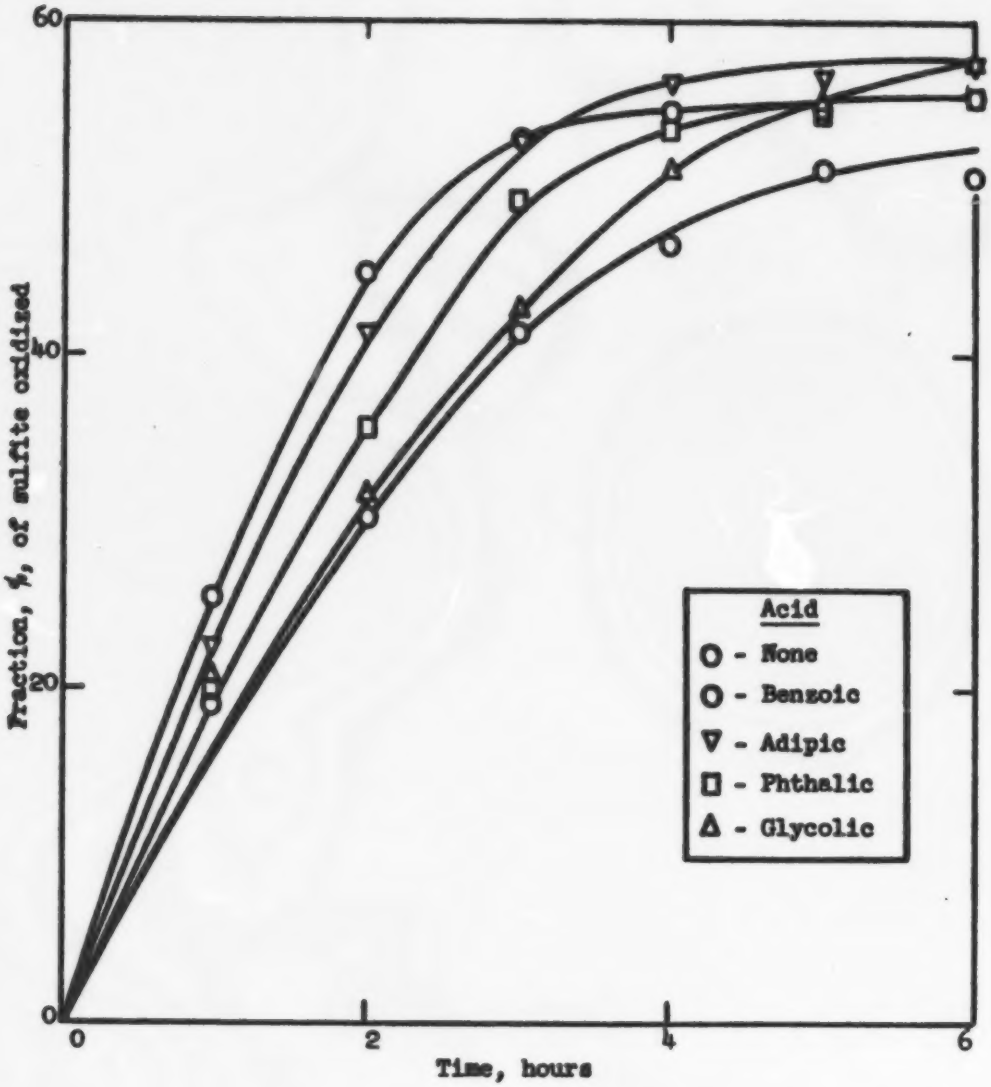


Figure 2

Effect of Organic Acid on the Oxidation of Sulfite to Sulfate in the Sodium System at 55°C

(J. D. Hatfield, Y. K. Kim,
M. E. Deming, R. L. Dunn)

Work done under OAP-TVA Contract No. TV-34425A

May 1971 - FR

Oxidation of Calcium Sulfite

The addition of organic acid to sodium sulfate solutions resulted in an increase in the rate of oxidation of sulfite to sulfate by oxygen gas at 55°C (May report), and the following order of increase was established: benzoic > adipic > phthalic > glycolic > no acid. In these tests, however, the concentrations of Na and S were 2.12 and 1.69 molal, respectively, and the presence of organic acid gave a buffering effect to the solution as the oxidation proceeded.

This report concerns oxidation studies in the calcium system at 50°C in which the concentration of S is much smaller than in the sodium system, because of solubility, and in which the buffering effect of the organic additive would be expected to be more pronounced. The effects of changing pH, constant pH, addition of organic additives, and the organic acid concentration (benzoic only) were studied.

The first tests were made under conditions similar to those used in the sodium system. The solutions were prepared by mixing 0.3 gram of powdered reagent $CaCO_3$ with 500 ml of water and adjusting the pH of the solution to about 4.0 by slowly absorbing gaseous SO_2 into the solution; the $CaCO_3$ dissolved completely. After purging the solution at 50°C with nitrogen gas at the rate of 20 ml/min, oxygen was added at a rate of 21 ml/min through a coarse fritted glass to a gas absorber that contained 400 ml of the solution. Samples (10 ml) were removed at intervals, and the total sulfite and pH were determined as quickly as possible to prevent further oxidation. The values for pH, total sulfite, and total calcium were used in a computer program to calculate the species concentrations and activities, using the constants and activity coefficients suggested by the Radian Corporation (PB 193029). The partial pressure of CO_2 was varied in the calculations from 0.0 to 0.0003 atmosphere, but this did not affect the distribution of calcium and sulfur species because most of the CO_2 is present in these solutions as dissolved CO_2 (or H_2CO_3). An example of the computer printout is given in Table I for the sample taken at 1 hour in run I. The water lost due to the flowing oxygen was calculated from its vapor pressure and the rate and time of gas flow; this was used to correct the calcium and total sulfur concentrations for the various times. The sulfur volatilized was obtained by a mass balance between the initial total sulfur content and the sum of the sulfite and sulfate; this was superior to integrating the partial pressure of SO_2 curve with time because of the rapid rise in SO_2 pressure as the pH decreased.

TABLE I

Distribution of Aqueous Species and the Properties of the Solution During the Oxidation of Sulfite to Sulfate With Oxygen at 50°C

	SPECIES	ACTIVITY	MOLALITY	ACT.COEFF
1	H2O			0.99970
2	H	0.8511E-03	0.9616E-03	0.8851E+00
3	OH	0.6438E-10	0.7405E-10	0.8695E+00
4	H2SO3	0.8085E-03	0.8059E-03	0.1003E+01
5	HSO3	0.7436E-02	0.8540E-02	0.8707E+00
6	SO3	0.3722E-06	0.6475E-06	0.5748E+00
7	HSO4	0.1403E-03	0.1614E-03	0.8695E+00
8	SO4	0.7978E-03	0.1434E-02	0.5562E+00
9	H2CO3	0.0000E+00	0.0000E+00	0.1003E+01
10	HCO3	0.0000E+00	0.0000E+00	0.8707E+00
11	CO3	0.0000E+00	0.0000E+00	0.5748E+00
12	CA	0.3077E-02	0.5305E-02	0.5801E+00
13	CAOH	0.5522E-11	0.6351E-11	0.8695E+00
14	CASO3	0.3670E-05	0.3658E-05	0.1003E+01
15	CASO4	0.6953E-03	0.6931E-03	0.1003E+01
16	CACO3	0.0000E+00	0.0000E+00	0.1003E+01
17	CAHCO3	0.0000E+00	0.0000E+00	0.8695E+00

T=	1.0	PH=	3.07	TCA=	0.00600
TSO2=	0.00935	TSO3=	0.00229	TCO2=	0.0000E+00
PSO2=	0.1507E-02	PCO2=	0.0000E+00	PH2O=	0.1217E+00
SV=	0.00019	HV=	0.1004		
EN=	0.21E-10	RR=	0.254875		
I=	0.1831E-01				

TCA, TSO_2, TSO_3, TCO_2 = total concentrations of components, molalities.
PSO_2, PCO_2, PH_2O = partial pressure of component, atmospheres.
SV = Sulfur volatilized, moles/KgH_2O.
HV = Water volatilized, grams.
EN = Electroneutrality check on solution of equations.
RR = $a_{HSO_3}/(a_H)^{1/2}$.
I = Ionic strength.

Three runs were made under conditions as constant as possible, and the results are shown in Figure 1 (runs I, II, and III). The initial pH of the solution ranged from 4.00 to 4.13, and the oxidation that occurred during preparation of the solutions ranged from 1.9 to 5.1% of the total sulfur. The total calcium molality was 0.006 and the initial total sulfur molality varied from 0.0116 to 0.01185. The pH of the solutions decreased rapidly at first and then decreased more slowly as the sulfate content increased. The initial oxidation rate decreased with time perhaps due to the decreasing sulfite content and to the effect of pH. The rate of oxidation of the three solutions (I, II, and III) appeared to be different, but the pH patterns of the solutions appeared to be identical.

A similar run (IV) was made with a solution containing 0.16% benzoic acid. The added benzoic acid was neutralized by addition of 0.0064 mole of calcium carbonate per kg of H_2O to keep the pH constant, with the sulfite concentration similar to that in runs I, II, and III. The pH change and the rate of oxidation for run IV are shown in Figure 1 by the dashed curves. The oxidation was much slower in the solution containing benzoic acid, reaching about 15% of the sulfite oxidized in 5 hours as compared to about 55% oxidation in the absence of benzoic acid. The pH did not fall as rapidly in the presence of benzoic acid because of the lower oxidation rate and the buffering effect of the additive.

A series of tests was made to determine the effect of pH on the rate of oxidation. The starting concentrations of sulfite ranged between 0.0114 and 0.0130 molal but with different amounts of $CaCO_3$ to give different pH values. After purging with nitrogen as before and starting the flow of oxygen (21 cc/min) into the solution maintained at 50°C, the pH was maintained constant throughout the run by the addition of small amounts of powdered $CaCO_3$. The results of runs made in the absence of organic additive are shown in Table II. The pH of the last run listed in Table II could not be held constant because the oxidation was so rapid that excess $CaCO_3$ was added, causing the pH to increase gradually during the run from 6.1 to 7.45.

The results in Table II are shown in Figure 2 as a first-order mechanism. This implies, at constant pH,

$$-dS_t/dt = kS_t \qquad (1)$$

where

k = specific reaction rate, sec^{-1}

t = time, sec

S_t = total sulfite concentration, m

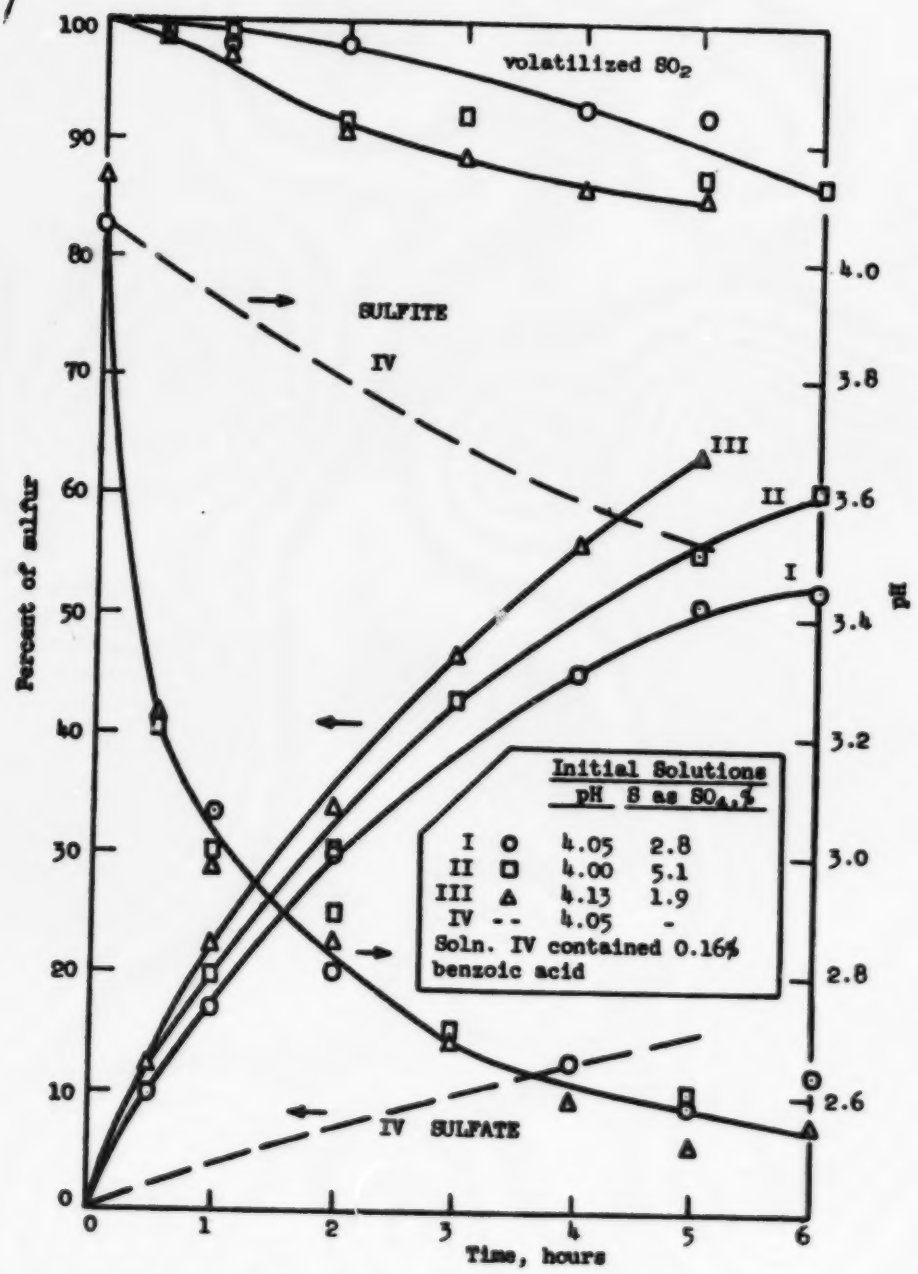


Figure 1

The Oxidation of Sulfite to Sulfate in the System CaO-SO_2-SO_3-H_2O at 50°C With O_2 Gas

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TABLE II

Effect of pH on the Rate of Oxidation in Calcium-Bisulfite-Sulfite System With O_2 at 50°C

pH	Time, hours	Fraction oxidized, %	k, sec^{-1}
3	0	0	5.66×10^{-6}
	0.5	2.5	
	1	5.4	
	2	13.0	
	3	22.8	
	4	22.7	
	5	37.9	
	6	48.3	
3.5	0	0	1.72×10^{-5}
	0.5	6.1	
	1	20.4	
	2	43.2	
	3	59.0	
	4	70.4	
4.0	0	0	4.31×10^{-5}
	0.5	18.6	
	1	44.0	
	2	79.5	
	3	89.5	
4.5	0	0	1.03×10^{-4}
	0.5	34.8	
	1	76.0	
	1.5	99.0	
6.10	0	0	1.16×10^{-4}
6.45	0.5	40.3	
7.10	1	87.0	
7.45	2	~100	

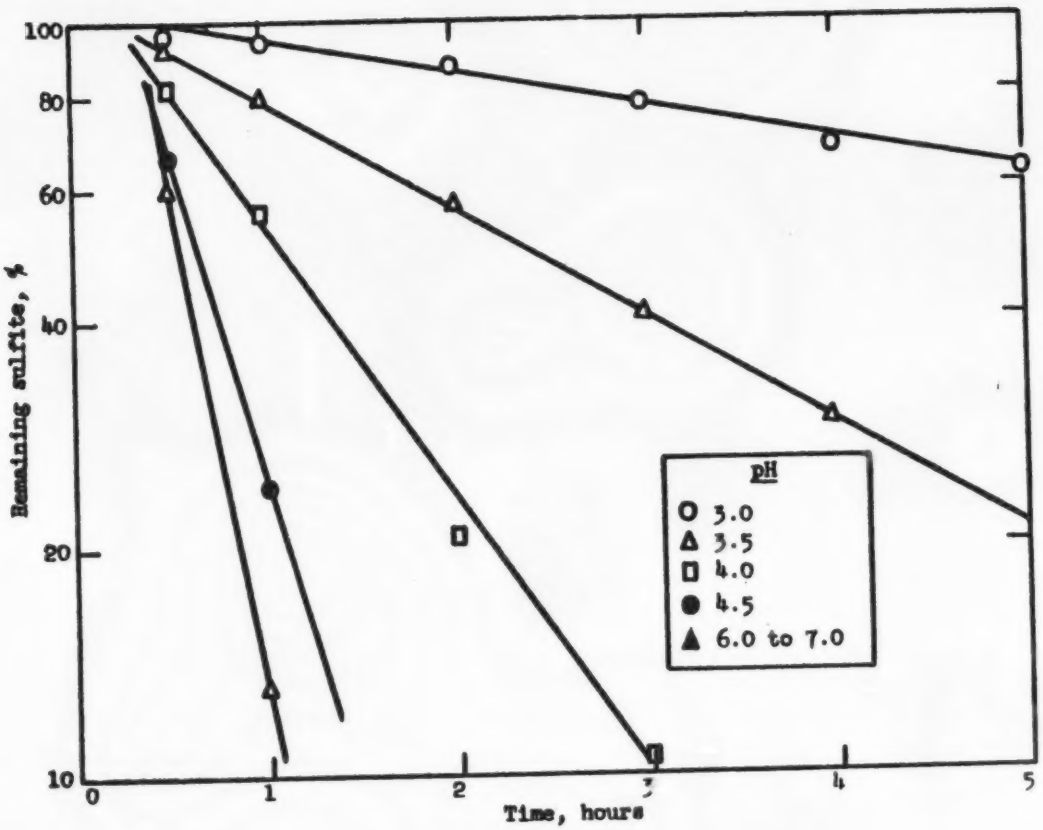

Figure 2

Effect of pH on the Oxidation of Sulfite to Sulfate in Calcium System at 50°C

The integral form

$$\log (S_t/St^\circ) = -kt/2.303 \qquad (2)$$

indicates that the slopes of the lines (Figure 2) are equal to $-k/2.303$ for each experimental condition. The values of k are listed in the last column of Table II. The magnitude of k is directly proportional to the oxidation rate.

The value of the total sulfite, S_t, can be expressed by

$$S_t = SO_3^{2-} + HSO_3^- + H_2SO_3 + CaSO_3 \qquad (3)$$

Omitting the negligible amount of $CaSO_3$, and using the ionization constants of the H_2SO_3, K, and K_2,

$$S_t = (HSO_3^-)\{[K_2/(H^+)] + 1 + [(H^+)/K_1]\} \qquad (4)$$

Therefore $dS_t/dt \propto d(HSO_3^-)/dt$ at constant pH.

If the oxidation rate is related to the pH in a simple relation, then

$$dS_t/dt = k'S_t(H^+)^n \qquad (5)$$

where

$$k = k'(H^+)^n \qquad (6)$$

or

$$\log k = \log k' - npH \qquad (7)$$

The values of k in Table II are plotted in Figure 3 according to equation 7. The relation is almost linear between pH 3 and 4.5 with a slope of about -1; at the highest pH the relation is obscured perhaps by the difficulty in maintaining constant pH. The oxidation rate in the high pH range may be influenced also by the presence of precipitated $CaSO_3$ and other solids which make the system heterogeneous instead of homogeneous. Consequently the oxidation rate at the high pH should be considered differently. For the system in the pH range 3 to 4.5, the oxidation rate may be expressed by equation 5 with n = -1.

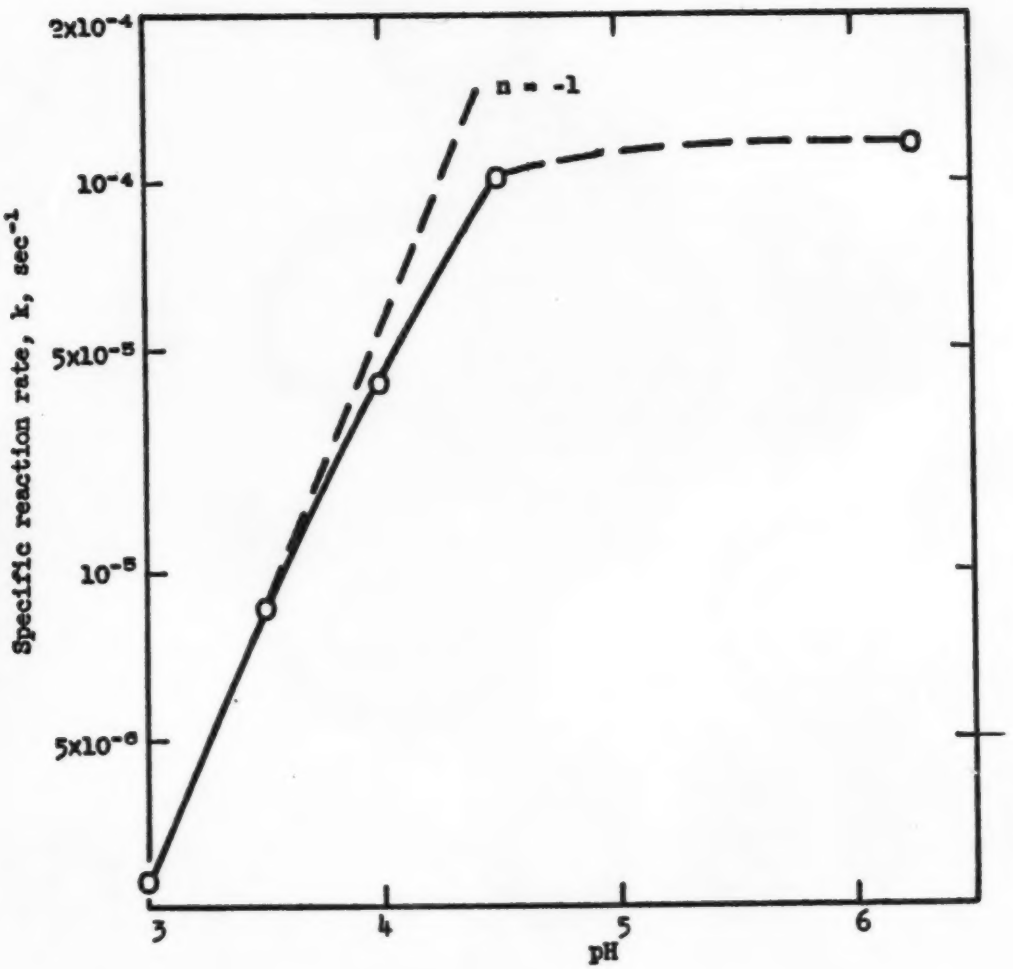

Figure 3

Effect of pH on the Oxidation Rate

of $CaSO_3$-$Ca(HSO_3)_2$ at 50°C

A series of tests was made to compare the four organic acids (benzoic, phthalic, glycolic, and adipic) at constant pH. The test solution was prepared by suspending 0.3 gram $CaCO_3$ in 500 ml H_2O and absorbing SO_2 gas so that the final solution had a pH of 4.0 and a total sulfite concentration of 0.0123 m. Then 0.5 gram of each organic acid was added to portions of the above solution and the pH adjusted to 4.0 by adding appropriate amounts of $CaCO_3$. After purging with nitrogen for about 40 minutes at 50°C, pure oxygen was introduced at the rate of 21 ml/min through the same apparatus. The pH of the solution was maintained constant at 4.0 during the run by adding powdered $CaCO_3$ as needed; 10-ml samples were taken at intervals for determination of the total sulfite concentration by iodine titration.

The same straight-line relationship was found between log total sulfite in the solution and time (Figure 4). The specific reaction velocity values, k, are listed in Table III. All the organic acids tested retarded the oxidation of sulfite to sulfate by oxygen gas at pH 4.0 and 50°C in the order benzoic > glycolic > phthalic > adipic > no acid.

The effect of the concentration of benzoic acid on the specific rate constant for oxidation at 50°C and pH 4 is shown in Figure 5. The lower the concentration of benzoic acid, the smaller the effect of oxidation retardation, and finally at about 0.0003% benzoic acid the effect was not detectable. The concentration effect may be expressed empirically by

$$k = k^{\circ}A/(A + Bm)$$

where $A = 4 \times 10^{-4}$, $B = 0.5$, m = benzoic acid concentration, and k° = reaction rate constant when $m = 0$.

Our results definitely indicate that all four organic acids behave as oxidation inhibitors to the oxidation of sulfite by pure O_2; this is contrary to the pilot-plant results using flue gases (May 1970 Applied Research Branch report). Further study will be made to clarify this discrepancy and to determine the mechanism of the oxidation.

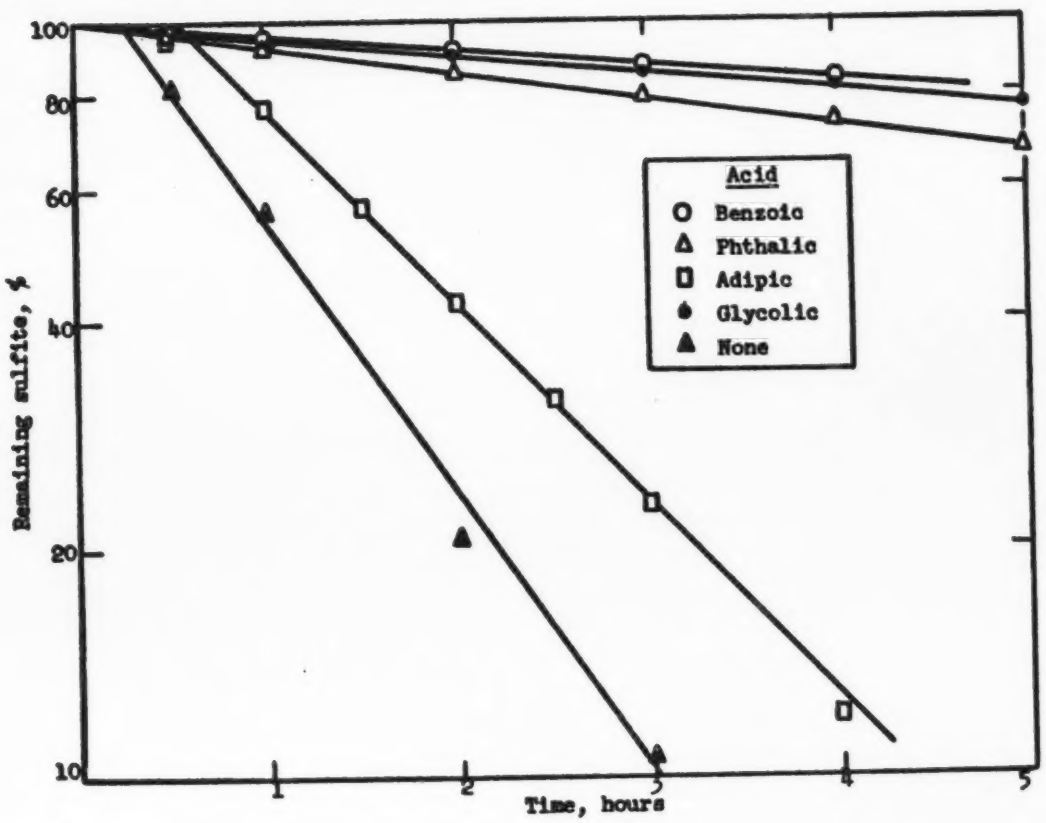

Figure 4

Effect of Organic Acids on the Oxidation of Sulfite to Sulfate in Calcium System at 50°C and pH 4.0

TABLE III

Effect of Organic Acids on the Rate of Oxidation in the Calcium Sulfite-Bisulfite System at pH 4 and 50°C

Acid	Concn., %	Time, hours	Fraction oxidized, %	k, sec^{-1}
Benzoic	3.2×10^{-3}	0	0	1.89×10^{-5}
		0.5	7.0	
		1	21.4	
		1.5	35.3	
		2	44.5	
		3	53.5	
Benzoic	0.1	0	0	2.36×10^{-6}
		0.5	1.7	
		1	4.3	
		2	8.5	
		3	12.6	
		4	16.2	
Phthalic	0.1	0	0	4.25×10^{-6}
		0.5	2.6	
		1	7.6	
		2	14.2	
		3	21.1	
		4	27.3	
		5	32.4	
Glycolic	0.1	0	0	2.93×10^{-6}
		0.5	2.5	
		1	5.0	
		2	10.0	
		3	15.0	
		4	19.0	
		5	24.0	
		6	27.2	
Adipic	0.1	0	0	3.20×10^{-5}
		0.5	5.4	
		1	23.2	
		1.5	43.4	
		2	57.9	
		2.5	68.6	
		3	77.1	
		4	88.0	

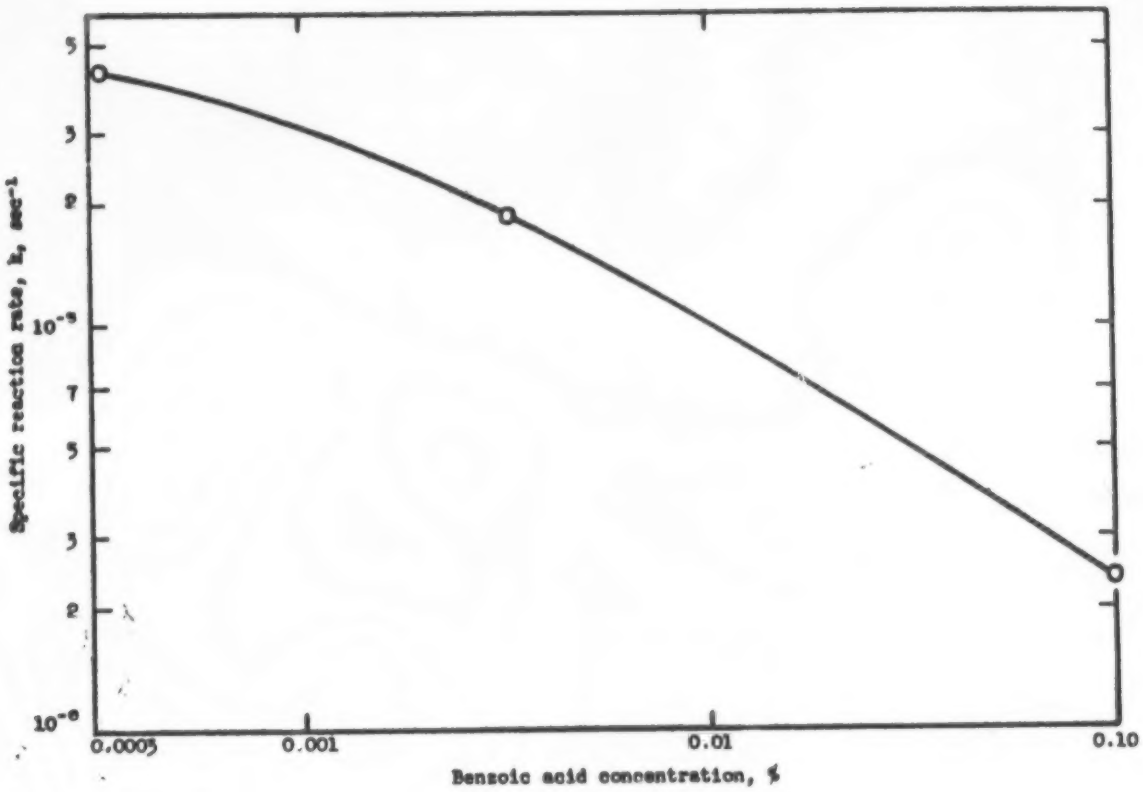

Figure 5

Effect of Benzoic Acid Concentration on the
Oxidation of Sulfite to Sulfate in Calcium System at 50°C and pH = 4.0

(J. D. Hatfield, Y. K. Kim,
M. E. Deming, R. L. Dunn)

Effect of Benzoic Acid on the Oxidation of Sulfite: In pilot-plant studies (Applied Research Branch report, May 1970) in which simulated flue gas containing sulfur dioxide and oxygen was passed through an aqueous suspension of limestone, addition of benzoic acid to the suspension increased the oxidation of sulfite to sulfate. In our laboratory studies, in which oxygen was bubbled through solutions of sulfites or bisulfites, benzoic acid increased the oxidation of sodium sulfite (May report) but decreased the oxidation of calcium sulfite (July report). In further laboratory studies of the effect of benzoic acid on the oxidation of sulfite, mixtures of sulfur dioxide and oxygen were bubbled through aqueous suspensions of powdered reagent calcium carbonate.

A mixture of sulfur dioxide (1.4 ml/min), oxygen (6.5 ml/min), and nitrogen (63 ml/min) was bubbled through 500 ml of water at 50°C in a 1-liter reaction vessel until the pH dropped to 4.0. The gas flow was maintained for 3 hours and the pH was held at 4.0 ± 0.1 by addition of small amounts of powdered calcium carbonate. The sulfite sulfur in solution was determined by iodine titration of 10-ml samples that were withdrawn periodically. The exit gas from the reaction flask contained no detectable sulfur dioxide, and the sulfate sulfur in the suspension was obtained by difference. The test was repeated under the same conditions except that the initial water contained 0.1% benzoic acid. As shown in Table III, with no benzoic acid 35 to 40% of the sulfite was oxidized, whereas only 7 to 14% was oxidized in the presence of benzoic acid. If all the oxidation is assumed to be that of the SO_2 added between samplings, the rate of oxidation is lowered by benzoic acid, as shown in the last column of Table III.

In a similar test made for 5 hours with a mixture of the same flows of sulfur dioxide and nitrogen but with 17 ml/min of oxygen, 0.1% benzoic acid was added after the gas had been passed for 3.5 hours. The amounts of sulfate found, run 2 in Table III, indicate that benzoic acid retards the oxidation of sulfite at the higher oxygen flow rate also. Although benzoic acid retards the oxidation of sulfite under these conditions, increasing the amount of oxygen in the gas increases the oxidation, but not enough to overcome the effect of the benzoic acid.

TABLE III

Effect of Benzoic Acid on the Oxidation of Sulfite in the Presence of Calcium at 50°C

(Gas mixture of 1.4 ml/min SO_2, 63 ml/min N_2, and O_2 bubbled through suspension; $CaCO_3$ added as required to maintain pH 4)

Run No.	Benzoic acid concn., %	Time, hr	Concn., M, x 10^2 of S		SO_4 S, % of total S	Fraction, %, of SO_2 added during sampling period that was oxidized to SO_4^{2-}
			Total	As SO_4^{2-}		
			O_2 flow, 6.5 ml/min			
1A	0.0	1	0.75	0.48	36.0	36.0
		2	1.515	0.98	35.4	34.6
		3	2.295	1.395	39.2	46.8
1B	0.1	1	0.75	0.695	7.3	7.3
		2	1.515	1.37	9.5	11.7
		3	2.295	1.978	13.8	22.0
			O_2 flow, 17.0 ml/min			
2	0.0	1	0.75	0.62	17.3	17.3
		2	1.515	0.99	34.6	52.
		3	2.295	1.03	55.2	95.
	0.1	3.5	2.705	1.07	60.5	90.
		4	3.11	1.345	56.8	34.0
		4.5	3.54	1.635	53.8	32.5
		5	3.98	1.96	50.8	25.0